THE UNIVERSITY OF ALBERTA

Hydrates of Methane-Propylene and Methane-Ethylene Mixtures

by

Frederick Douglas Otto

FACULTY OF ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

January 1959

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Hydrates of Methane-Propylene and Methane-Ethylene Mixtures

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
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BY

FREDERICK DOUGLAS OTTO

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ABSTRACT

The conditions at which methane-ethylene and methane-propylene mixtures form solid hydrates in the presence of liquid water have been determined for pressures up to 2000 lb/in.^{2}abs. Experimental data for the vapor, hydrate and water-rich liquid equilibrium in the ethylene-water system have been extended from 867 to 2000 lb/in.^{2}abs.

Solid-vapor equilibrium ratios were calculated for ethylene and propylene. A comparison between predicted and actual hydrate forming conditions for a methane-ethylene-propylene mixture showed that these equilibrium ratios must be used cautiously.

Schematic phase diagrams are presented which depict the phase relations peculiar to the methane-propylene-water system.

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Table of Contents

Page No.

List of Tables i

List of Figures ii

List of Symbols iv

I. INTRODUCTION 1

II. LITERATURE REVIEW 3

(1) Historical Aspects 3

(2) Previous Work on Systems Under Investigation 7

(a) Methane-Water System 7
(b) Ethylene-Water System 7
(c) Propylene-Water System 9

(3) Non-Equilibrium Behavior of Gas Hydrates 12

(4) Composition of Hydrocarbon Hydrates 13

(a) Pure Hydrocarbon Hydrates 13
(b) Mixed Hydrocarbon Hydrates 14

III. THEORY 16

(1) Phase Rule -- General Considerations 16

(2) Two Component Phase Equilibria 17

(3) Three Component Phase Equilibria 28

(4) Significance of the Dew Point to the Formation of Hydrates 30

(5) Vapor-Solid Equilibrium Ratios 31

IV. EXPERIMENTAL 37

(1) Experimental Apparatus 37

(a) Equilibrium Cell 37
(b) Measurement and Control of Phase Variables 39
(i) Temperature 39
(ii) Pressure 40
(c) Assembly of Apparatus 41
(d) Materials Used 41

Table of Contents (continued ..)

(2) Experimental Technique 43

(a) Hydrate Formation 43
(b) Hydrate Equilibria 43
(c) Sampling and Analytical Procedure 45

V. EXPERIMENTAL RESULTS 46

(1) Experimental Phase Equilibrium Data for Binary Systems 46

(a) Methane-Water System 46
(b) Ethylene-Water System 48
(c) Propylene-Water System 48

(2) Experimental Phase Equilibrium Data for Ternary Systems 51

(a) Methane-Ethylene-Water System 51
(b) Methane-Propylene-Water System 56

(3) Hydrate Behavior 60

(4) Critical Phenomena in CH_4-C_3H_6-H_2O System 62

(5) Correlation of Experimental Data 63

(6) Phase Diagrams for the Methane-Propylene-Water System 69

VI. DISCUSSION 79

(1) Validity of Experimental Data 79

(2) Ethylene-Water System 79

(3) Ternary Systems 80

(4) Solid-Vapor Equilibrium Ratios 81

VII. FUTURE WORK 83

Bibliography 84

Appendix 86
Experimental Data 87
Calculated Data 92
Sample Calculations 98

List of Tables

Table		Page No.
I	Published Temperatures and Pressures for Formation of Methane Hydrate	8
II	Published Temperatures and Pressures for Formation of Ethylene Hydrate	10
III	Pressure-Temperature Data of Reamer, Selleck and Sage for Propylene-Water	11
IV	Experimental Pressure-Temperature Data for Methane-Water	87
V	Experimental Pressure-Temperature Data for Ethylene-Water H-L_1-V Equilibrium	88
VI	Experimental Pressure-Temperature Data for Propylene-Water V-L_1-L_2 Equilibrium	88
VII	Experimental Data for Three-Phase Equilibria, H-L_1-V, in the CH_4-C_2H_4-H_2O System	89
VIII	Four-Phase Equilibrium Data for Methane-Propylene-Water System	90
IX	Experimental Data for Three-Phase Equilibria, H-L_1-V, in the CH_4-C_3H_6-H_2O System	91
X	Calculated Solid-Vapor Equilibrium Ratios for Ethylene	92
XI	Calculated Solid-Vapor Equilibrium Ratios for Propylene	95
XII	Comparison of Calculated with Experimental Conditions for Hydrate Formation	97

List of Figures

Figure		Page No.
1	Previously Published Data on Hydrate Forming Conditions for Hydrocarbon Gases, CO_2 and H_2S	6
2	Hydrate Equilibria for Binary Hydrocarbon-Water System where System is Above Critical Temperature of Hydrocarbon	18
3	Hydrate Equilibria for Binary Hydrocarbon-Water System Where System is Below Critical Temperature of Hydrocarbon	19
4	Pressure-Temperature Projection for Hydrocarbon-Water System where Hydrate Equilibria Exist Above the Hydrocarbon Critical Temperature	24
5	Pressure-Temperature Projection for Hydrocarbon-Water System where Hydrate Equilibria Exist Below the Hydrocarbon Critical Temperature	25
6	Constant Pressure Temperature-Composition Diagrams	26
7	Dew Point Curves for CH_4-H_2O	29
8	Solid-Vapor Equilibrium Ratios for Methane	33
9	Schematic Apparatus Assembly	36
10	Equilibrium Cell	38
11	Experimental Apparatus	42
12	Conditions for Hydrate Formation in Methane-Water System	47
13	Conditions for Hydrate Formation in Ethylene-Water System	49
14	Conditions for Hydrate Formation in Propylene-Water System	50

List of Figures (continued ..)

15 Conditions for Hydrate Formation in Methane-Ethylene-Water System 52

16 Hydrate Formation Conditions for Methane-Ethylene Mixtures 55

17 Conditions for Hydrate Formation in Methane-Propylene-Water System 57

18 Hydrate Formation Conditions for Methane-Propylene Mixtures 58

19 Solid-Vapor Equilibrium Ratios for Ethylene 65

20 Solid-Vapor Equilibrium Ratios for Propylene 66

21 Comparison of Calculated with Experimental Conditions for Hydrate Formation 68

22 Boundary of Space Diagram for Methane-Propylene-Water System at 450 lb/in.^{2}abs. 71

23 Schematic Constant Temperature Sections for Methane-Propylene-Water System at 450 lb/in.^{2}abs. 72

24 Boundary of Space Diagram for Methane-Propylene-Water System at 1500 lb/in.^{2}abs. 76

25 Schematic Constant Temperature Sections for Methane-Propylene-Water System at 1500 lb/in.^{2}abs. 77

List of Symbols

n	Number of moles
F	Number of degrees of freedom
C	Number of components
P	Pressure; in phase rule -- number of phases
T	Temperature
V	Vapor
S	Solid hydrocarbon
I	Ice
L_2	Hydrocarbon-rich liquid
L_1	Water-rich liquid
H	Hydrate
K	Equilibrium ratio
y	Mole fraction of component in vapor phase
x	Mole fraction of component in liquid phase
z	mole fraction of component in hydrate

I. INTRODUCTION

A number of gases, including the C_1 to C_4 paraffinic and olefinic hydrocarbon gases, when under pressure and in the presence of water, will form solid hydrates. For example, methane appears to react with approximately seven molecules of water to form a solid crystal resembling snow or ice, that is

$$CH_4\ (\text{gas}) + 7H_2O\ (\text{liquid}) \longrightarrow CH_4 \cdot 7H_2O\ (\text{solid})$$

The temperatures, at which hydrates will form, are dependent upon pressure and may extend considerably above 32°F.

The industrial importance of this phenomenon was first realized in 1934 when Hammerschmidt (7) informed the natural gas industry that the formation of solid compounds of methane, ethane, propane and butane and water were responsible for the plugging of natural gas transmission lines. More generally, hydrate formation may occur in any equipment involved in the production, transmission and processing of light hydrocarbon gases where liquid water may be present along with favorable conditions of temperature and pressure. The solid hydrate will accumulate at low spots in pipe lines or around valves and fittings until the lines may become entirely plugged.

Prevention of liquid water deposition, and consequently hydrate formation, is ordinarily accomplished by dehydration of the gas. To determine when and to what extent the gas should be dehydrated, it is necessary to know the conditions of temperature and pressure at which hydrate formation is possible, as well as to have equilibrium moisture content data for the gas.

Hydrate forming conditions have been investigated for many pure hydrocarbon gases and for many different natural gases. Katz (1) and his co-workers, at the University of Michigan, have prepared a correlation which can be used to predict hydrate forming conditions for mixtures of the components generally found in natural gases; namely C_1 to C_4 paraffinic hydrocarbons, hydrogen sulfide and carbon dioxide.

Although ethylene and propylene are known to form hydrates no previous attempt has been made to include these gases in the above mentioned correlation. This, along with the fact that ethylene and propylene are common components of many process gas streams in industrial petro-chemical plants, has warranted a further investigation of hydrate forming conditions for these pure unsaturated hydrocarbon gases and for mixtures of gases containing these olefins.

This report describes an investigation of the hydrate equilibria in the methane-ethylene-water system, the methane-propylene-water system and associated binary hydrocarbon-water systems. These systems were chosen so that the experimental data could be used to include ethylene and propylene in a correlation of the type developed by Katz (1).

II. LITERATURE REVIEW

(1) Historical Aspects

The first experimental investigations of the formation of hydrates in gas-water systems are adequately reviewed by Katz and Rzasa (8), Hammerschmidt (7) and by Schroeder (18). According to these sources, Humphrey Davy in 1810 discovered the first known hydrate, a crystalline compound formed from chlorine and water. Cailletet in 1878 reported acetylene hydrate and was the first to discover that a sudden decrease in pressure aided in the formation of these crystalline compounds. Woehler in 1840 reported a hydrate of hydrogen sulfide. Villard (21,22), working in the period between 1880-1900, made an extensive experimental study of gas hydrates including the determination of decomposition curves of methane, ethane and ethylene hydrates. De Forcrand (6), working during the same period, was the first to attempt the determination of the composition of hydrates by thermodynamic methods. No further work was reported on gas hydrates until 1934, when Hammerschmidt (7) related hydrate formation to the freezing of natural gas transmission lines. He obtained experimental data on hydrate formation conditions for a number of natural gases and investigated ways of preventing their formation.

Hammerschmidt's work touched off a renewed interest in gas hydrates and a number of workers have since contributed greatly to this field. Deaton and Frost (2,3) studied decomposition curves for a

number of natural gases as well as for methane, ethane, propane and mixtures of methane with various concentrations of other hydrocarbons. They also attempted to determine the composition of paraffinic hydrates and found pressure-temperature data for several pure gases below 32°F (4). Roberts et al. (14,15), in 1940 and 1941, presented an excellent discussion of the methane-water and ethane-water systems. Katz et al. have contributed significantly to the hydrate field. Wilcox, Carson and Katz (23,1), in 1941, introduced vapor-solid equilibrium constants, for use in calculating and predicting hydrate forming conditions for natural gases. Carson and Katz (1) studied the methane-propane-water, methane-pentane-water and methane-hexane-water systems. Their results indicated that the paraffin hydrocarbons formed solid solutions. They also found no evidence for the existence of hydrates of the pentanes and heavier hydrocarbons. Kobayashi and Katz (9) studied the methane hydrate at high pressures. Unruh and Katz (20) investigated hydrates in the methane-carbon dioxide-water system and Noaker and Katz (10) studied the methane-hydrogen sulfide-water system. Reamer, Selleck and Sage (13) in 1952 studied the propane-water and propylene-water systems in the hydrate region and, in addition, obtained limited data on the propane-propylene-water system. An extensive study of the ethylene-water system was undertaken by Diepen and Scheffer (5) in 1950.

Parent (12) made a very complete appraisal of the technical and patent literature pertaining to the reaction of paraffinic hydrocarbon

gases with water to form solid hydrates and to the storage and subsequent decomposition of these substances. He concluded that there is an inadequate amount of data available in the published literature to permit a plant design; there being a need for quantitative rate data, heat capacities and pressure-temperature equilibrium data for more typical natural gases. However he felt that the process involving the formation of hydrocarbon hydrates from natural gas and water at times of low demand for the gas, followed by storage and subsequent regasification during the peak load season, appeared to warrant further investigation.

The basic method of preventing hydrate formation in a gas is dehydration. A number of investigators (7,17,19), beginning with Hammerschmidt (7) in 1934, have studied methods of dehydration.

Figure 1 is a temperature-pressure plot showing hydrate equilibrium curves that have been determined for binary hydrocarbon-water systems. Curves are also shown for two nonhydrocarbon hydrate forming components of natural gas; hydrogen sulfide and carbon dioxide. The equilibrium curves shown depict the temperatures and pressures at which the respective gases will form hydrates in the presence of water. The curves for n-butane and i-butane are dotted because reliable experimental data do not exist. The range of temperatures and pressures for their hydrate equilibria is very narrow and the formation of ice interferes with the crystallization of a solid hydrate phase and masks any hydrate that my be formed.

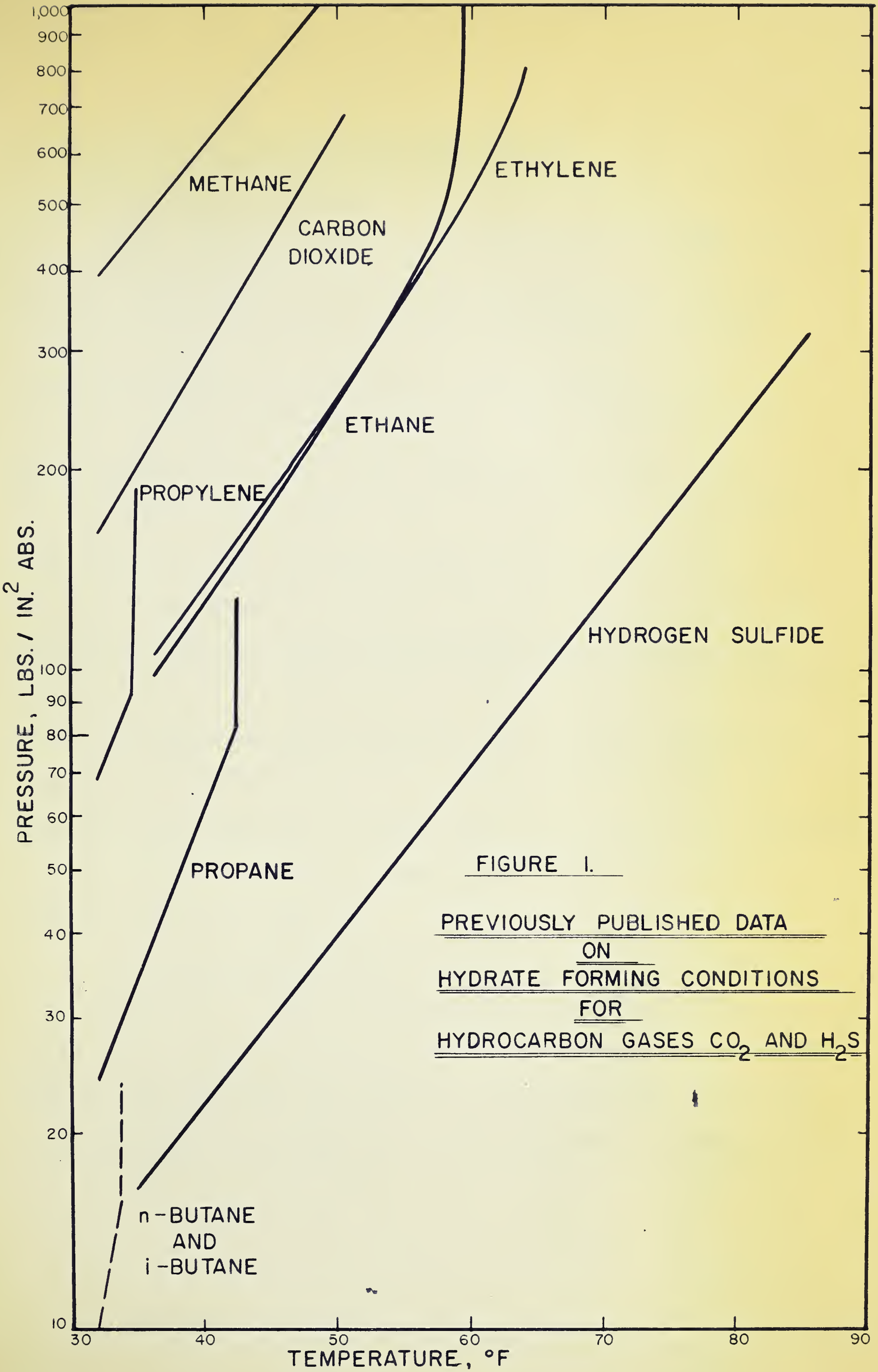


FIGURE I.

PREVIOUSLY PUBLISHED DATA ON HYDRATE FORMING CONDITIONS FOR HYDROCARBON GASES CO_2 AND H_2S

(2) Previous Work on Systems Under Investigation

(a) Methane-Water System

Villard (21,22) published data on methane hydrate in 1888. The data was considered quite reliable. He worked over a very wide range of pressures and temperatures and stated that 70.7°F was the highest temperature at which the solid hydrate could be formed. Deaton and Frost (3), in 1940, published more data for this system in the temperature range of 33°F to 55°F. Their sample was 99.7 percent methane and 0.3 percent carbon dioxide. Roberts et al. (14,15) reported some data in 1940 and 1941. The methane used was 99.9 percent pure. In 1946 Deaton and Frost (3) reported data for the vapor, ice and hydrate equilibrium. Finally, in 1948, Kobayashi and Katz (9) reported the results of a study of methane hydrate at pressures up to 11,200 lb/in.^{2}abs. Their work disproved Villard's postulate that a critical decomposition temperature of 70.7°F existed for this system. By extrapolating the data of Katz and Kobayashi, it appears that a pressure of 40,000 lb/in.^{2}abs. will cause hydrate to form at a temperature of 100°F. The published data are presented in Table I.

(b) Ethylene-Water System

Villard (21,22) was the first to obtain some data for this system and he reported experimental data for the three-phase equilibrium, hydrate, vapor and water-rich liquid, at temperatures from 32°F to 63°F and pressures from 95.5 lb/in.^{2}abs. to 867 lb/in.^{2}abs. By extrapolating

TABLE I

PUBLISHED TEMPERATURES AND PRESSURES FOR FORMATION OF METHANE HYDRATE

Author	Villard (21,22)		Deaton & Frost (3,4)		Roberts et al (14,15)		Kobayashi & Katz	
Phases	T (°F)	P (psia)	T (°F)	P (psia)	T (°F)	P (psia)	T (°F)	P (psia)
Vapor, Aqueous-liquid and Hydrate	32.0	390	33.0	401	32.0	383	72.6	4,930
	34.0	441	34.0	421	46.0	848	72.9	5,120
	41.9	690	36.0	470	56.0	1,542	82.1	9,400
	47.3	934	37.0	496	56.4	1,567	83.9	11,240
	49.8	1,102	39.0	553				
	51.4	1,220	43.0	692				
	57.7	1,813	45.0	776				
	61.0	2,235	46.0	828				
	63.1	2,620	47.0	879				
	66.7	3,410	49.0	982				
	68.5	3,900	52.0	1,178				
			55.0	1,419				
Hydrate, Ice and Vapor			12.6	260	6.6	239		
			15.9	276				
			20.0	302				
			23.8	322				
			28.0	347				

his data, Villard reported a critical decomposition temperature of 65.7°F for this system. Diepen and Scheffer (5) reported data for the three-phase equilibria, vapor, ice and hydrate and vapor, water-rich liquid and hydrate, from 5°F to 64.4°F, at pressures up to 793 lb/in.^{2}abs. They also reported data for the metastable equilibria, vapor, hydrocarbon-rich liquid and water-rich liquid, and hydrate, hydrocarbon-rich liquid and vapor. Reamer, Selleck and Sage (13) reported some data for this system but their data is somewhat scattered and does not agree very well with the data of (21,22) and (5). The published data for this system are presented in Table II.

(c) Propylene-Water System

Reamer, Selleck and Sage (12) reported the data given in Table III. They made experimental equilibrium measurements for the following three-phase equilibria: vapor, water-rich liquid and hydrate; water-rich liquid, hydrocarbon-rich liquid and hydrate; water-rich liquid, hydrocarbon liquid and vapor. The critical temperature of pure propylene is 196.8°F so that a liquid hydrocarbon layer can exist in this system at ordinary temperatures. The formation of this hydrocarbon liquid terminates the hydrate, water-rich liquid, vapor equilibrium at approximately 91 lb/in.^{2}abs. and 34.5°F. The highest temperature at which hydrate can exist in this system appears to be approximately 35.5°F, which is the approximate limiting temperature for the hydrate, water-rich liquid and hydrocarbon-rich liquid equilibrium.

TABLE II

PUBLISHED TEMPERATURES AND PRESSURES FOR FORMATION OF ETHYLENE HYDRATE

Author	Villard (21,22)		Diepen and Scheffer (5)		Reamer, Selleck and Sage (13)	
Phases	T (°F)	P (psia)	T (°F)	P (psia)	T (°F)	P (psia)
Vapor, Aqueous-liquid and Hydrate	32.0	95.5	32.0	81.5	32.0	91.0
	37.4	125	32.4	82.4	34.6	99.3
	41.9	162	32.7	83.9	34.7	143.6
	46.4	206	33.1	87.4	39.0	127.0
	51.8	309	33.4	87.6	41.3	179.9
	56.1	418	34.2	91.4	41.3	171.5
	58.6	507	34.5	93.3	42.0	203.6
	61.8	662	34.9	95.6	43.0	257.3
	63.0	867	35.6	99.4	43.7	302.4
			36.1	103	43.7	226.4
			36.7	106	45.1	280.9
			37.8	113.5	46.3	258.6
			37.8	113	47.4	322.2
			39.9	131	47.9	302.6
			41.7	150	49.3	349.5
			44.1	174	49.5	362.6
			47.7	218	50.4	335.3
			51.8	288	50.5	427.7
			54.9	364	52.6	402.3
			57.6	435	52.7	454.0
			59.5	498	53.7	474.9
			61.5	586	54.7	440.2
			62.4	642	55.3	513.3
			63.6	713		
			64.4	793		
Vapor, Ice and Hydrate			30.2	77.2		
			28.4	74.5		
			26.6	71.4		
			24.8	69.2		
			24.8	69.3		

TABLE III

PRESSURE-TEMPERATURE DATA OF REAMER, SELLECK AND SAGE FOR PROPYLENE-WATER

Temperature °F	Pressure lb/in.^{2}abs.	Phases
32.9	74.9	Hydrate, Aqueous-liquid, and Vapor.
33.4	78.6	
34.1	88.5	
41.0	98.6	Vapor, Aqueous-liquid, and Hydrocarbon-liquid.
39.6	100.9	
57.4	129.0	
59.4	132.6	
73.4	159.8	
98.2	34.5	Hydrate, Aqueous-liquid, and Hydrocarbon-liquid.
207.7	34.9	
308.3	35.2	

(3) Non-Equilibrium Behavior of Gas Hydrates

Hammerschmidt (7) made the following significant observations regarding hydrate formation:

> "The formation of gas hydrates in natural gas pipe lines depends primarily upon the pressure, temperature and composition of the gas-water vapor mixture. After these primary conditions are fulfilled, the formation of the hydrate is accelerated by high velocities of the gas stream, pressure pulsations or innoculation with a small crystal of the hydrate."

Deaton and Frost (2) observed that hydrate may not form even though the pressure is 300 to 400 lb/in.^{2}abs. above the decomposition temperature. They found that even violent agitation failed to initiate hydrate formation when the pressure was only slightly above the equilibrium value. They also observed,

> "In making the hydrate tests it has been observed that although most of the hydrate decomposes readily when the pressure in the cell is reduced at constant temperature, a small, indefinite amount of hydrate persists for a considerable time, even after the pressure is reduced to atmospheric. This hydrate which fails to decompose is submerged in the water or covered by a water film."

In general most workers have indicated that it is difficult to form hydrates even when well into the region for hydrate existence, and that the decomposition is by no means instantaneous when pressure is released. This behavior is not peculiar to hydrocarbon-water systems, but is characteristic of many phase changes and the general behavior of crystal formation.

(4) Composition of Hydrocarbon Hydrates

(a) Pure Hydrocarbon Hydrates

The compositions of pure hydrocarbon hydrates have not been definitely established. Difficulty in completely isolating the solid hydrate phase from coexisting phases, so that its composition can be determined, is largely responsible for the uncertainty existing as to the number of molecules of water which react with a hydrocarbon gas to form hydrate.

$$R + nH_2O \longrightarrow R \cdot nH_2O$$

where R is a hydrocarbon gas capable of forming a hydrate, with n molecules of water to every molecule of R.

Hydrates tend to occlude water during their formation and this, along with any adsorption or solid solution effects, makes it difficult to determine n definitely. Experimentally determined values of n generally vary from six to eight (4,13).

Parent (12) states:

> "It would appear likely that the hydrocarbon hydrates are isomorphous and that they should have the same ultimate structure. Villard held this view in 1888, and others since have believed it, but no one has clearly established the composition of any one of the hydrates, or that they are all isomorphous ..... If isomorphism can be established, and if the composition of any one of the hydrates can be established beyond doubt, then the composition of all the hydrates will be known."

However, it is also possible that hydrocarbon hydrates are mixtures of hexahydrates, heptahydrates, etc., or are of somewhat indefinite composition due to solid solution effects.

Several workers (6,7,14,5) have investigated thermodynamic methods for determining the hydrate composition. These methods are subject to a number of approximations but give values of n in the same range as those obtained by chemical methods.

(b) Mixed Hydrocarbon Hydrates

Katz and his co-workers based their development of the solid-vapor equilibrium ratio concept, for the prediction of hydrate forming conditions in natural gases, on the belief that the various hydrocarbon hydrates form solid solutions in each other. They obtained evidence with which to substantiate this belief. Carson and Katz (1) studied the four-phase, vapor, water-rich liquid, hydrocarbon-rich liquid and hydrate, equilibrium data for the methane-propane-water system and found that there was one degree of freedom; that is, their data fell on a single continuous curve on a pressure-temperature diagram. According to the phase rule the system comprised four phases since there were three components present. Since two liquid layers were visible, and a vapor phase existed, three phases were readily accounted for. This meant that the solids which were observed were all the same phase. It was concluded, then, that the single solid phase was likely to be a solid solution of methane hydrate and propane hydrate.

Carson and Katz also measured the concentration of methane and propane in the hydrate and found that the composition changed continuously along the four-phase equilibrium line. This indicated that the

single phase hydrate gradually changed in composition. Hammerschmidt (7) and Wilcox, Carson and Katz (23) noted that gas given off during the decomposition of natural gas hydrates had a gradually increasing density.

> "This behavior is characteristic of solid solutions and indicates that natural gas hydrates are likely to be solid solutions" (1).

As previously mentioned Carson and Katz found no evidence to indicate that the pentanes and higher hydrocarbons enter into the solid solution. They found that the addition of propane to the methane-water system displaced the pressure-temperature curve for the hydrate in the direction of the curve for propane. However, the addition of either pentane or hexane did not alter the hydrate equilibrium for the methane-water system and these components behaved only as inert diluents. Deaton and Frost (3) showed that the addition of either iso- or normal butane shifted the hydrate equilibrium curve. Parent (12) suggests that if solid solutions are formed then the hydrates are probably isomorphous

> "since this is the normal requirement for extensive solubility of one solid substance in another."

Thus, it seems probable that mixed hydrocarbon gases will form hydrates which are solid solutions in each other and that the pentanes and higher hydrocarbon gases will not be present in the hydrate crystal, except for that which may be present due to occlusion or adsorption effects. These hydrates may also be of the same ultimate structure. For example, they may all be heptahydrates.

III. THEORY

(1) Phase Rule - General Considerations

The phase rule states that if a heterogeneous system consisting of C components in P phases is in equilibrium then

$$F = C - P + 2$$

where F is the number of degrees of freedom, or the smallest number of independent variables that must be specified in order to define completely the remaining variables in the system. In using the phase rule as expressed by the above equation the only variables to be considered are temperature, pressure and composition.

Conventional phase diagrams may be used to represent the phase relations in hydrocarbon-water systems. The following generalities help in constructing these diagrams (16).

> "The addition of a component to a system adds a degree of freedom to all features represented for the system. In other words, lines will generate surfaces and points will generate lines. These features will have one extra degree of freedom but will not be changed in designation. That is, a point representing vapor, solid and liquid in equilibrium for a one component system will generate a line in space on the addition of a second component, but this line will represent equilibrium between the same phases. Similarly, a line representing vapor-liquid equilibrium will generate a surface which will represent a liquid saturated with vapor. Associated with each surface there must be another surface representing vapor saturated with a liquid."

Phase equilibria can be terminated in three ways:

1. by addition of a phase,
2. loss of a component, or
3. by critical behavior where two phases become identical.

(2) Two Component Phase Equilibria

Single hydrocarbons in the presence of water form two component systems. The conditions at which three phases are in equilibrium in a two component system are represented by a three-phase line, since a two component system in three phases has only one degree of freedom. For a two component system in two phases, two degrees of freedom exist and are seen as areas on the phase diagram. These areas are defined by the three-phase equilibrium lines bounding the individual areas.

Conventional pressure-temperature projections, such as Figure 2 and Figure 3, may be used to represent the two possible types of phase diagrams that may exist for hydrocarbon-water systems. The type of diagram for each particular system depends mainly on the behavior of the pure hydrocarbon at different temperatures and pressures. The first type is represented by Figure 2 which is typical for systems where the pure hydrocarbon is above its critical point at the temperatures and pressures under consideration. Accordingly, only the hydrocarbon vapor can exist and there will be no region of two immiscible liquids. The systems methane-water and ethylene-water are of this type.

The pressure-temperature projection in Figure 3 represents systems of the second type. In this case the hydrocarbon vapor is capable of condensation to a liquid phase and thus a hydrocarbon liquid shows up on the diagram. The systems ethane-water and propylene-water are of this type.

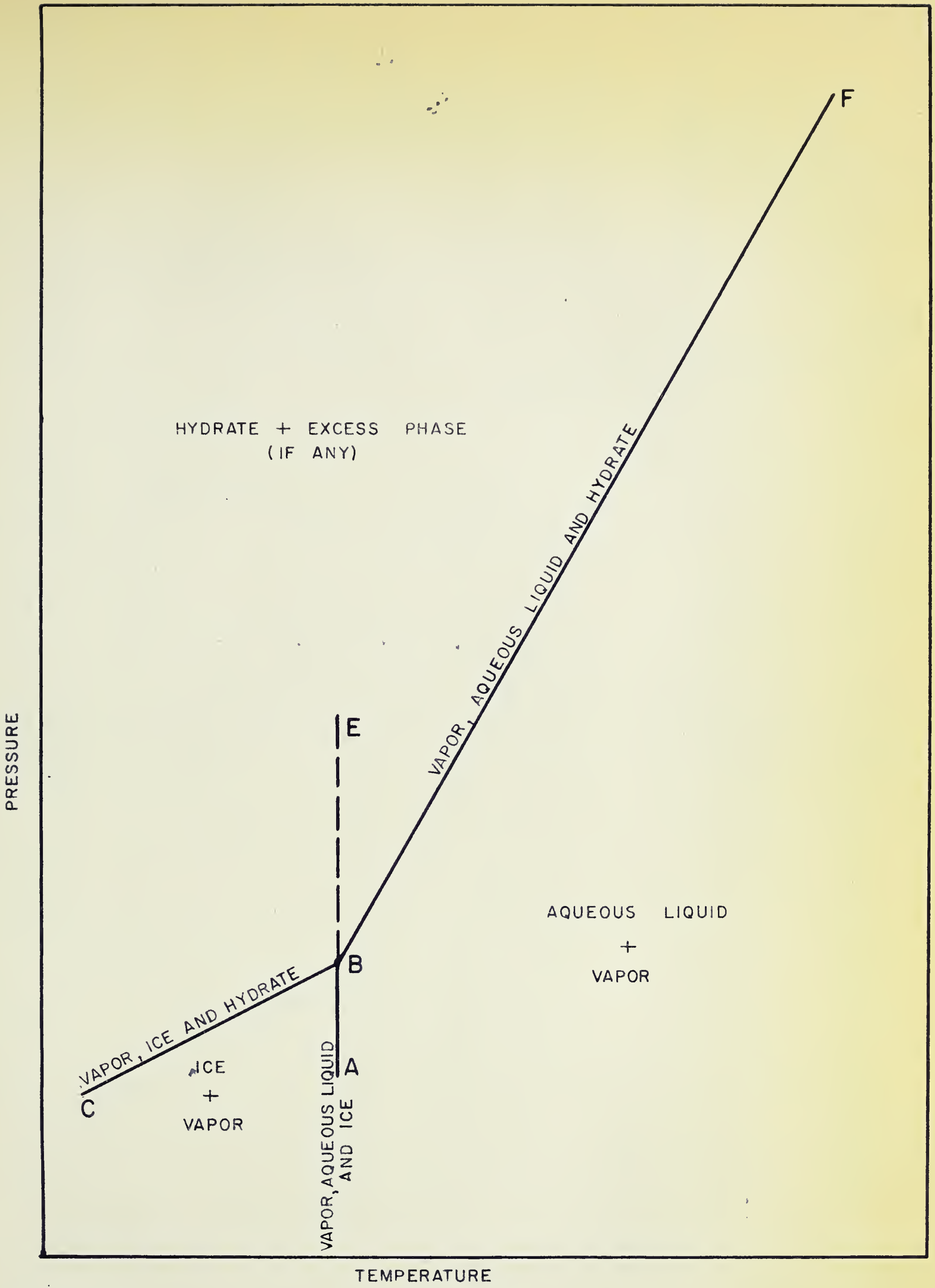

F
HYDRATE + EXCESS PHASE (IF ANY)
VAPOR, AQUEOUS LIQUID AND HYDRATE
E
PRESSURE
AQUEOUS LIQUID + VAPOR
B
VAPOR, ICE AND HYDRATE
ICE + VAPOR
A
C
VAPOR, AQUEOUS LIQUID AND ICE
TEMPERATURE

FIGURE 2.

HYDRATE EQUILIBRIA FOR BINARY HYDROCARBON-WATER SYSTEM WHERE SYSTEM IS ABOVE CRITICAL TEMPERATURE OF HYDROCARBON

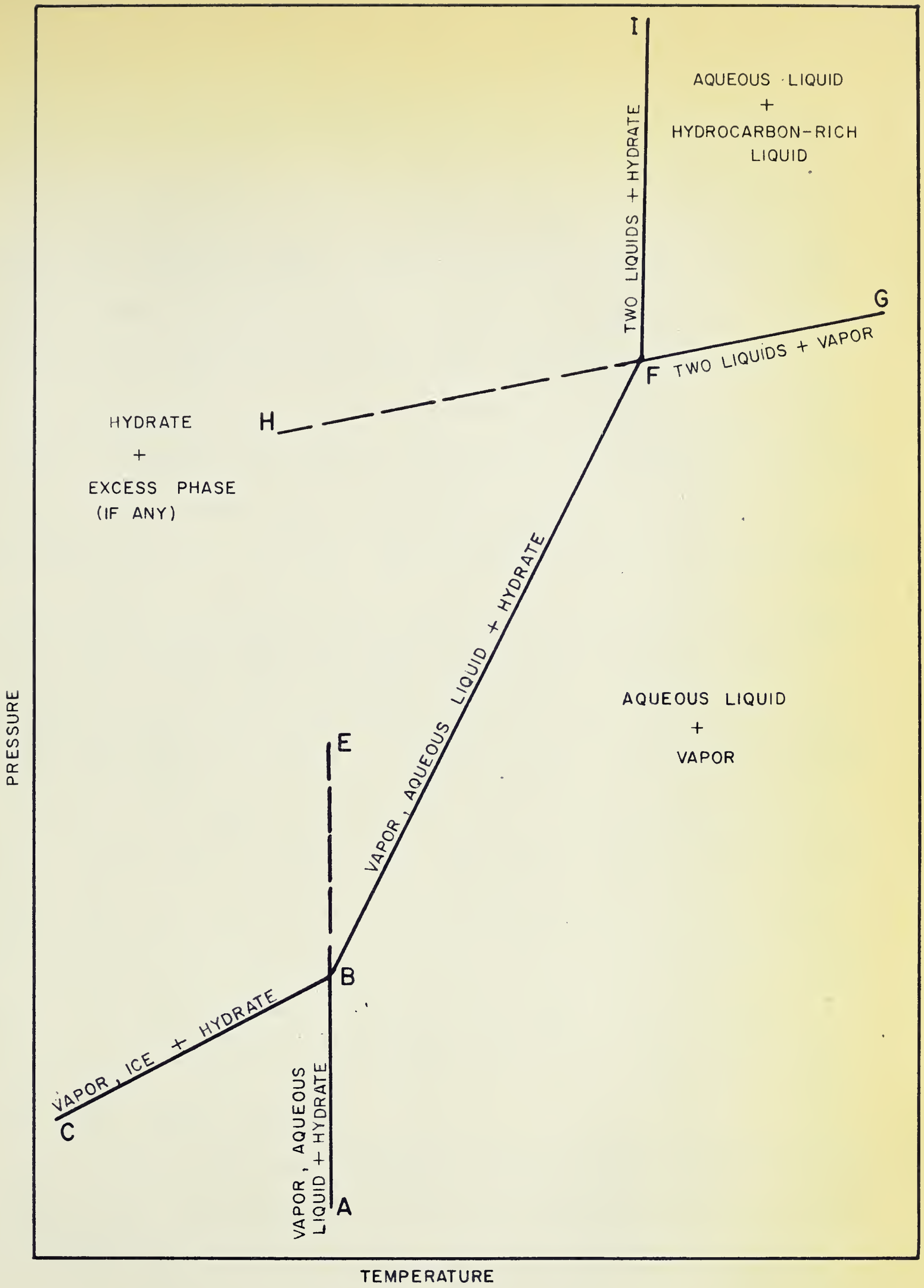

I
AQUEOUS LIQUID
+
HYDROCARBON-RICH
LIQUID
TWO LIQUIDS + HYDRATE
G
F
TWO LIQUIDS + VAPOR
HYDRATE
+
EXCESS PHASE
(IF ANY)
H
VAPOR, AQUEOUS LIQUID + HYDRATE
AQUEOUS LIQUID
+
VAPOR
PRESSURE
E
B
VAPOR, ICE + HYDRATE
C
VAPOR, AQUEOUS
LIQUID + HYDRATE
A
TEMPERATURE

FIGURE 3.

HYDRATE EQUILIBRIA FOR BINARY HYDROCARBON-WATER SYSTEM WHERE SYSTEM IS BELOW CRITICAL TEMPERATURE OF HYDOCARBON

Throughout this discussion the letter H denotes hydrate, I denotes ice, V denotes vapor, S denotes solid hydrocarbon, and L_2 and L_1 denote hydrocarbon-rich liquid and water-rich liquid respectively. In Figure 2, BF represents the three-phase equilibrium water-rich liquid, hydrate and vapor. This equilibrium is of special significance in that it represents the hydrate decomposition (or formation) curve for the hydrocarbon gas and water. Point B is approximately at 32°F and below this point ice will form. Hydrocarbons are generally only slightly soluble in water and thus cause no appreciable lowering of the freezing point. The freezing point line ABE is practically vertical, since a variation in pressure has very little effect on the freezing point. It is seen that hydrate can exist to the left of CBF. Other phases present to the left of CBF depend upon the mole ratio of hydrocarbon gas to water. If the ratio is exactly that required for hydrate formation only hydrate will exist. If there is excess water present, ice and hydrate will exist in the area above CB and to the left of BE, and hydrate and a liquid layer will exist above BF and to the right of BE. If excess hydrocarbon gas is present there will be hydrocarbon vapor and hydrate in the entire region above CBF.

In Figure 3, BF again represents the three-phase equilibrium VL_1H. As the pressure and temperature of the three phases are increased, point F is reached where a hydrocarbon-rich liquid is formed. At this point we have a quadruple point representing hydrocarbon-rich liquid, water-rich

liquid, vapor and solid hydrate existing in equilibrium at a single temperature and pressure. The conditions at which vapor, hydrocarbon-rich liquid and water-rich liquid exist in equilibrium are represented by FG. The line HFG can usually be approximated with the vapor pressure curve for the pure hydrocarbon as the presence of water affects it only slightly. HF represents the HL_2V equilibrium which exists only if there is an excess of hydrocarbon-rich liquid. HF may also represent a metastable equilibrium for VL_1L_2. FI represents the HL_1L_2 equilibrium. The effect of pressure on a condensed system is slight and thus the curve representing the HL_1L_2 equilibrium rises very steeply. It is seen that hydrate can exist to the left of CBFI. If the ratio of hydrocarbon and water corresponds to that required for hydrate formation, only the hydrate phase will exist in this region. If water is in excess, hydrate and liquid water will exist above BF, to the left of FI and to the right of BE, and hydrate and ice will exist above BC and to the left of BE. If excess hydrocarbon vapor is present, hydrate and hydrocarbon vapor will exist above CBF and below HF, and hydrocarbon liquid and hydrate will exist above HF and to the right of FI.

A more complete picture of the two types of phase diagrams can be obtained from diagrams such as those illustrated in Figure 4 and Figure 5. Here space curves, existing in three dimensional figures representing pressure, temperature and composition of the hydrocarbon-water systems, are projected on a pressure-temperature plane. These diagrams and the constant pressure sections to follow have been taken

from a report "Application of the Phase Rule to a Study of Natural Gas Hydrates" by Robinson (16). Temperatures and pressures of important features are located approximately in their correct relative positions. No attempt has been made to keep a uniform scale because of the wide range of pressures covered and the limited solubility of the hydrocarbons in water. The phase diagrams of pure water and pure hydrocarbon in one component system appear on the boundary planes of the three dimensional figures.

Point A is a quadruple point formed when the equilibrium, hydrocarbon solid, vapor and hydrocarbon-rich liquid, is terminated by the addition of a hydrate phase. The phase rule tells us that, if four phases are present, there must be at least four lines representing different three-phase equilibria, all intersecting at a point in the pressure-temperature projection. Then, associated with the above quadruple point will be three other space curves representing equilibrium between

1. Solid hydrocarbon, hydrate, vapor;
2. Hydrate, hydrocarbon-rich liquid, vapor; and
3. Hydrate, hydrocarbon-rich liquid, solid hydrocarbon.

On the water side of the diagram similar features arise and the quadruple point B represents ice, hydrate, water-rich liquid and vapor in equilibrium. The associated three-phase equilibria intersecting to form this point must be as follows:

(i) Vapor, ice, hydrate;
(ii) Vapor, hydrate, water-rich liquid;
(iii) Ice, water-rich liquid, hydrate; and
(iv) Vapor, ice and water-rich liquid.

For systems where the hydrate equilibria exist above the critical temperature of the pure hydrocarbon (Figure 4), the termination of the line representing hydrate, water-rich liquid and vapor is somewhat in doubt. Kobayashi and Katz (10) have determined this equilibrium, for the methane-water system, up to 11,200 lb/in.^{2}abs. and 84°F. Robinson (16) suggests that this equilibrium is terminated by a critical point where vapor and water-rich liquid become identical. If this is true, there will be a locus of points where vapor and water-rich liquid are identical, joining this critical with the critical for pure water. A similar situation arises where the hydrocarbon liquid and vapor become identical.

For systems where the hydrate equilibria exist below the critical temperature of the pure hydrocarbon (Figure 5), a quadruple point exists at point F because the three-phase equilibrium, L_2VH, intersects the L_1VH equilibrium at some temperature and pressure before critical behavior has been reached. Hence, the three-phase equilibrium, L_1VH, has been terminated by the addition of a phase, which is in this case L_2.

By drawing temperature-composition diagrams at constant pressures these systems may be described still more completely. Two typical diagrams are shown in Figure 6(a) and Figure 6(b). Each three-phase equilibrium line, cut by the plane of constant pressure, will appear on the temperature-composition diagram as an invariant temperature line drawn through three points; each point representing the fixed composition of a phase at that pressure and temperature.

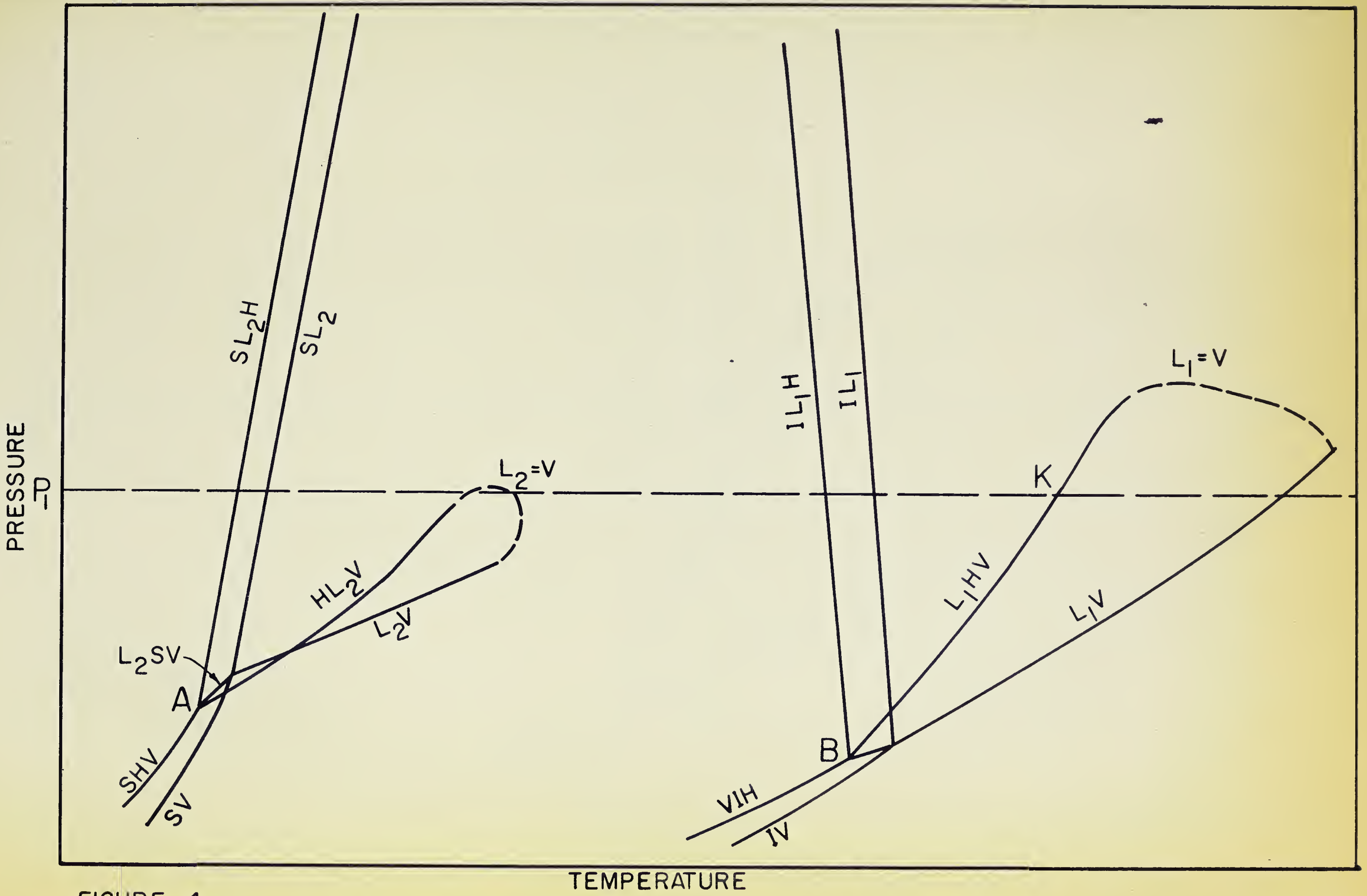

PRESSURE
P
TEMPERATURE
SL_2H
SL_2
IL_1H
IL_1
$L_1=V$
$L_2=V$
K
HL_2V
L_2V
L_1HV
L_1V
L_2SV
A
B
SHV
SV
VIH
IV

FIGURE 4

PRESSURE-TEMPERATURE PROJECTION FOR HYDROCARBON-WATER SYSTEM WHERE HYDRATE EQUILIBRIA EXIST ABOVE THE HYDROCARBON CRITICAL TEMPERATURE

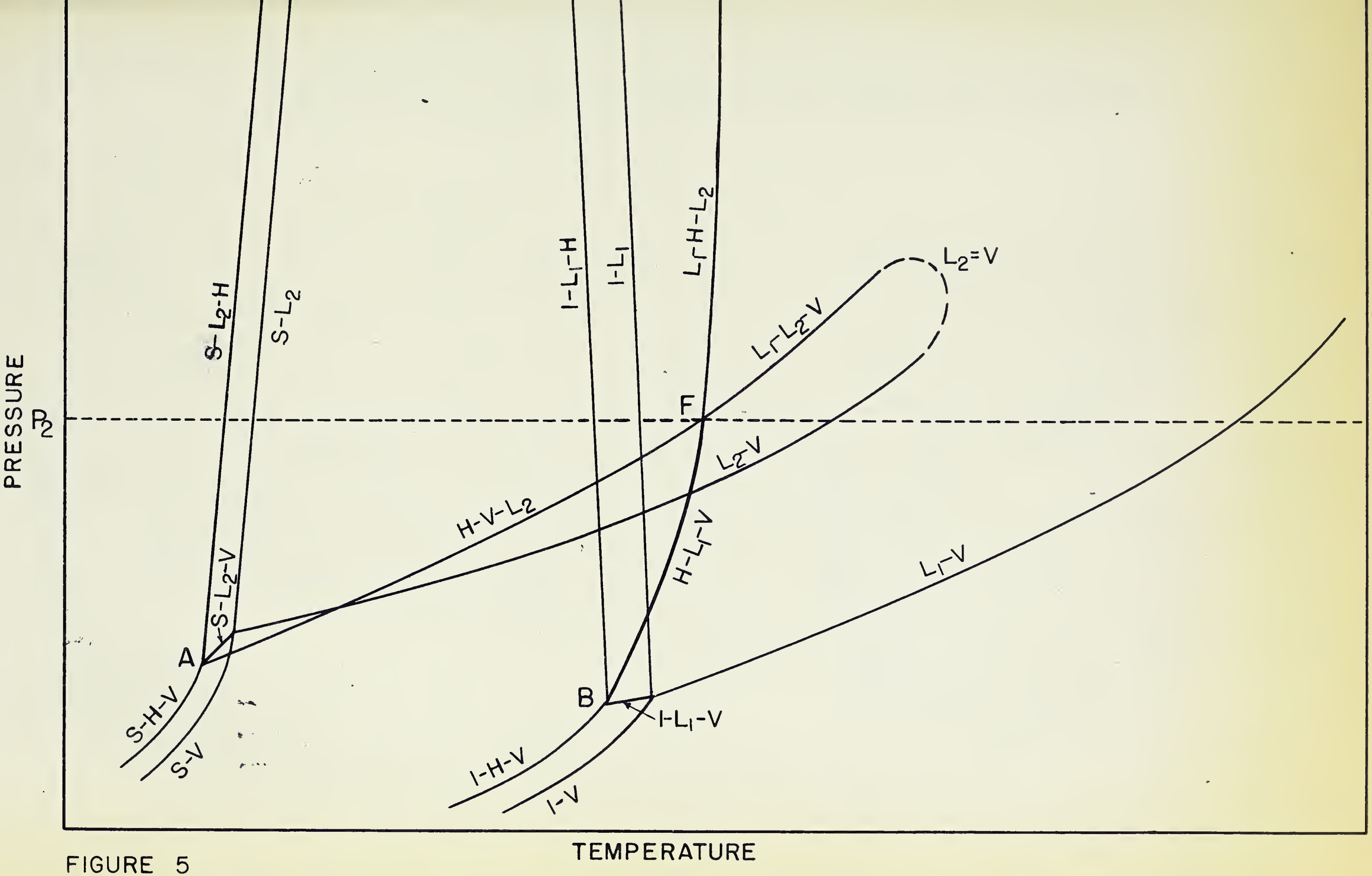

PRESSURE
P_2
TEMPERATURE
S-L_2-H
S-L_2
I-L_1-H
I-L_1
L_1-H-L_2
L_2=V
L_1-L_2-V
F
L_2-V
H-V-L_2
H-L_1-V
L_1-V
S-L_2-V
A
S-H-V
S-V
B
I-L_1-V
I-H-V
I-V

FIGURE 5
PRESSURE-TEMPERATURE PROJECTION FOR HYDROCARBON-WATER SYSTEM WHERE HYDRATE EQUILIBRIA EXIST BELOW THE HYDROCARBON CRITICAL TEMPERATURE.

FIG. 6 CONSTANT PRESSURE TEMPERATURE-COMPOSITION DIAGRAMS.

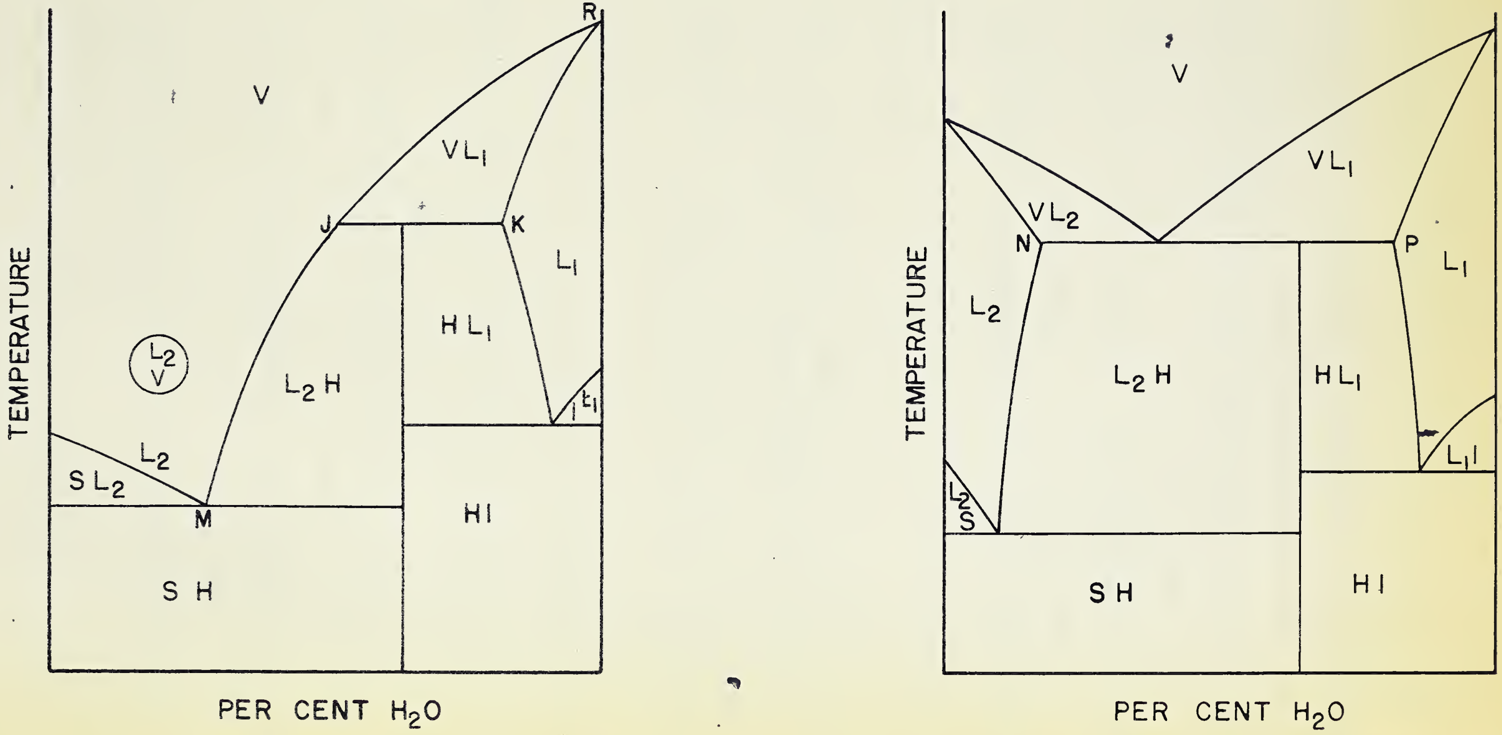

TEMPERATURE
PER CENT H_2O
R
V
VL_1
J
K
L_1
HL_1
L_2 V
L_2H
L_1I
L_2
SL_2
M
HI
SH
TEMPERATURE
PER CENT H_2O
V
VL_1
VL_2
N
P
L_1
L_2
L_2H
HL_1
L_1I
L_2S
SH
HI

FIG. 6(a) TEMPERATURE-COMPOSITION DIAGRAM AT P_1 ON FIGURE 4.

FIG. 6(b) TEMPERATURE-COMPOSITION DIAGRAM AT P_2 ON FIGURE 5.

The pressure of the system shown in Figure 6(a) is P_1 on Figure 4. The intersection of the constant pressure plane with the HVL_1 equilibrium at point K (Figure 4) is shown on Figure 6(a) by the three-phase invariant temperature line JK. This is the highest three-phase temperature possible for this system at this pressure. The disappearance of the hydrocarbon-rich liquid at this pressure is indicated by the small enclosed area representing the hydrocarbon-rich liquid, vapor equilibrium. The area is closed because the constant pressure plane crosses the locus of critical points twice.

Figure 6(b) is the temperature-composition diagram drawn for P_2 (Figure 5). This pressure plane passes through the quadruple point F. The four phases, hydrate, water-rich liquid, hydrocarbon-rich liquid and vapor are in equilibrium along the invariant temperature line NP shown on Figure 6(b).

Lines of real practical significance on these diagrams are the invariant temperature lines JK and NP, above which hydrate will not form, and the dew point lines represented by MJR on Figure 6(a). A discussion of the significance of dew point lines is given in Section III (4). These constant pressure, temperature-composition diagrams are also helpful in visualizing the three dimensional diagram, and illustrate the amount of information that can be obtained about a system from a pressure-temperature projection of space curves and application of phase rule principles.

(3) Three Component Phase Equilibria

A two component gas with water comprises a three component system. Application of the phase rule tells us that a three component system in one phase has four degrees of freedom, therefore, in order to represent such a system in three space coordinates, it is necessary to specify one variable as constant for the whole diagram. The variations in concentration of three component systems are conveniently represented in two dimensions by the use of triangular diagrams, which permit direct plotting of the two independent concentrations and the dependent concentration. These are constant temperature-constant pressure diagrams. A three dimensional model may then be constructed by representing temperature or pressure on a perpendicular to the plane of the triangular diagram. Thus, the complete isobaric or isothermic phase equilibrium model consists of a prism, the sides of which represent either the temperature-composition or the pressure-composition diagrams for each of the three binary systems.

For the three component system two degrees of freedom will exist for three-phase equilibria. Therefore, assuming that all hydrates formed are solid solutions, the vapor, water-rich liquid and hydrate equilibrium will show two degrees of freedom and hydrate, existing in a system of fixed total composition, can be expected to melt over a range of temperatures for a particular constant pressure. Only if a four-phase equilibrium such as vapor, hydrocarbon-rich liquid, water-rich liquid and hydrate exists will the system exhibit one degree of freedom.

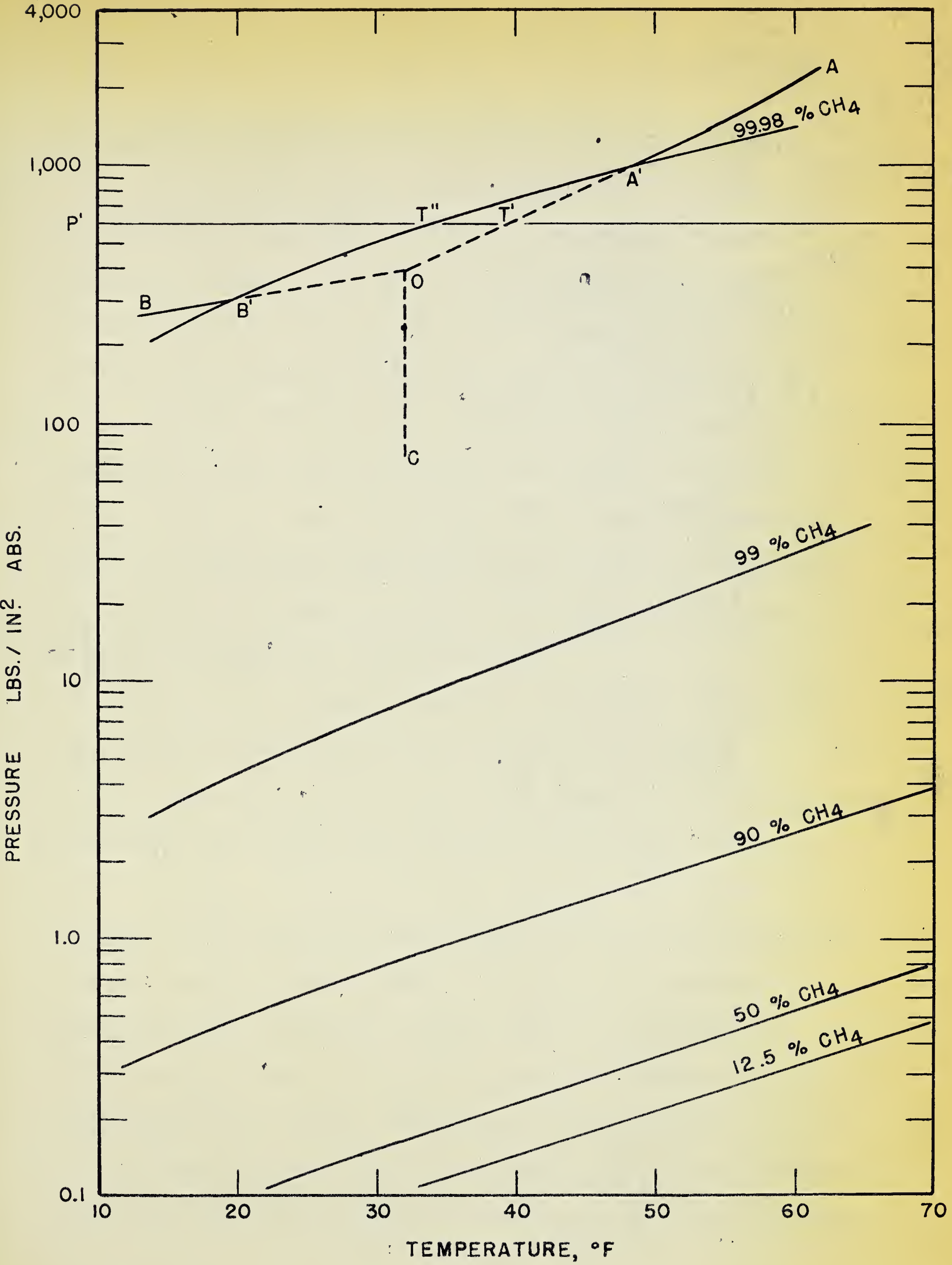


FIG. 7 DEW POINT CURVES FOR METHANE - WATER (14)

(4) Significance of the Dew Point to the Formation of Hydrates

The prevention of gas hydrates formation can ordinarily be accomplished by dehydration of the gas. This dehydration must be carried out at least to the point where condensation of water is prevented when in regions of pressure and temperature where hydrate can form. It is thus of considerable importance to consider dew point equilibria. The dew point is defined as the pressure and temperature at which water will begin to condense. For example, above the dew point line MJR in Figure 6(a), mixed hydrocarbon and water vapor exist only. Below the dew point line, water-rich liquid will condense and hydrate can form once the temperature is equal to or below the temperature represented by JK.

Figure 7 is a pressure-temperature projection of dew point curves for the methane-water system, along with the hydrate equilibria curves. Below the dew point lines on this figure, that is, at presures lower than the dew point pressures, methane and water will exist as a vapor. Above the dew point lines water-rich liquid will condense. It is seen that as the methane content of the system rises that the dew point curve is displaced toward higher pressures. An interesting case, which may be brought about by dehydration, is shown in Figure 7 where the 99.98 mole percent curve intersects the hydrate curve at A' and B'. For a system of this composition the parts of the equilibrium curves represented by OB', OA' and CO lie within the vapor region and therefore do not exist. Therefore, there

is a region, lying between temperatures corresponding to A' and B', respectively, where hydrate is formed directly from the vapor phase. For an operating pressure of P', hydrate formation will begin at T' if a water-rich liquid phase is present. If dehydration is carried out until the composition is 99.98 mole percent methane, hydration will not begin until a temperature of T'' is reached.

Diagrams of this type are useful as guides for adjusting operating conditions when working with hydrate forming gases under pressure and for predicting the amount of dehydration that will be most economical in any particular situation.

(5) Vapor-Solid Equilibrium Ratios

The equilibrium ratio K is used as a practical means of calculating vapor-liquid equilibria for hydrocarbon mixtures when the vapor does not behave ideally. The vapor-liquid equilibrium ratio K_{L-V}, for any component i, is defined as follows:

$$K_{L-V} = \frac{y_i}{x_i}$$

y_i is equal to the mole fraction of component i in the vapor phase and x_i is equal to the mole fraction of i in the liquid phase. K_{L-V} is, in general, a function of pressure, temperature and the nature and composition of the solution.

Wilcox, Carson and Katz (23,1) applied this equilibrium ratio concept to the vapor-solid equilibrium existing when solid hydrate forms in a multi-component gas-water system. They reasoned that if multi-component gas hydrates form solid solutions in each other then vapor-solid equilibrium should be somewhat analogous to vapor-liquid

equilibrium. Then, basing their calculations on the fact that experimental data indicate that mixed hydrocarbon hydrates are solid solutions, they prepared vapor-solid equilibrium ratios which have proven useful in predicting hydrate forming conditions in natural gases. They defined the vapor-solid equilibrium ratio as follows:

$$K_{V-S} = \frac{y}{z} = \frac{\text{mole fraction of hydrocarbon in vapor (dry basis)}}{\text{mole fraction of hydrocarbon in hydrate (dry basis)}}$$

Only the hydrocarbon portions of the vapor and solid phases are considered. These vapor-solid equilibrium ratios are used for computing hydration conditions in the same manner in which calculations are made for dew point, percent vaporization or bubble point for liquid-vapor systems.

Carson and Katz first determined vapor-solid equilibrium ratios for methane. They are given in Figure 8. To calculate these ratios they required composition data for gases containing methane and gases resulting from the decomposition of hydrates in equilibrium with these gases. They were able to obtain one point at each pressure up to 1,000 psia by using the hydrate composition data they collected when studying the four-phase equilibrium (VL_1L_2H) in the methane-propane-H_2O system. They assumed that water had only a small effect on the vapor-liquid equilibrium for the propane-methane system and used, for the vapor compositions, the composition of vapor in equilibrium with liquid in the propane-methane system at the same temperatures and pressures that the hydrate equilibria existed. They obtained one point at

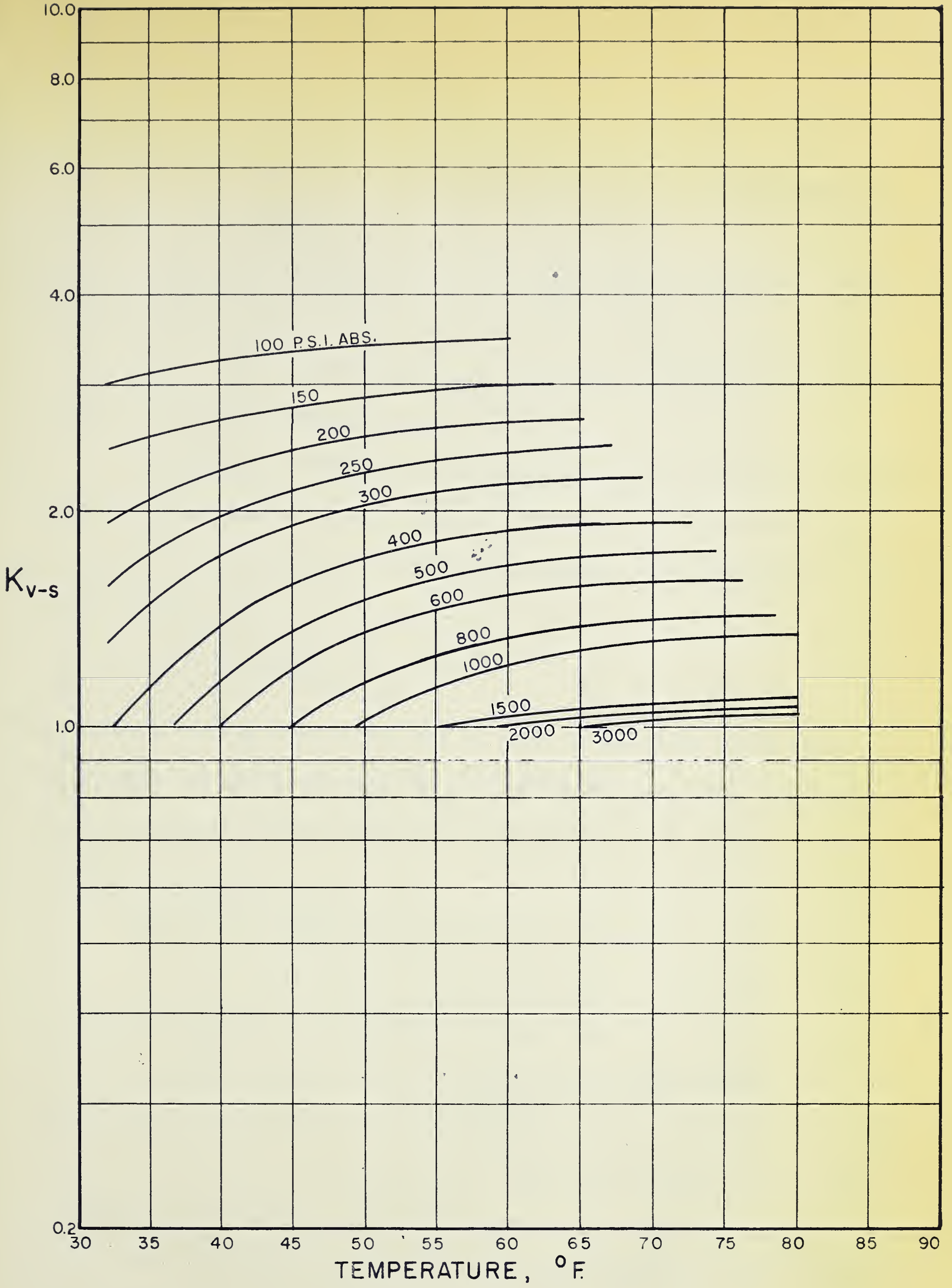


FIG. 8

SOLID-VAPOR EQUILIBRIUM RATIOS FOR METHANE (I)

600 lb/in.^{2}abs. from data Hammerschmidt reported for the decomposition of hydrate formed from a natural gas. They also knew that K equals one for points on the hydrate formation curve for pure methane. They then had three points for the 600 lb/in.^{2}abs. curve and so drew this curve first. Other curves were drawn in symmetrically and the range of pressures covered expanded by extrapolation.

To find K_{V-S} values for other gases it is not necessary to obtain hydrate composition data. If initial hydration points and vapor compositions are available for a binary gas system containing methane, the relationship,

$$\Sigma z = \Sigma \frac{y}{K_{V-S}} = 1$$

at hydrate forming conditions, may be used to calculate solid-vapor equilibrium ratios for the gas in the system with methane. The point at which hydrate initially forms corresponds to the dew point in vapor-liquid equilibrium.

Katz et al. (1,10,11) have published solid-vapor equilibrium ratio charts for components of natural gas known to contribute to the composition of natural gas hydrates. These charts are for methane, ethane, propane, n-butane, carbon dioxide and hydrogen sulfide. A comparison (1) of predicted and experimental values for several natural gases has shown that these vapor-solid equilibrium ratios may be used to predict the pressure of hydrate formation for a given pressure with an error of generally not more than 10%. Considering the various assumptions and extrapolations used to prepare these charts and the

fact that the solid phase probably does not behave ideally, this agreement is reasonably good.

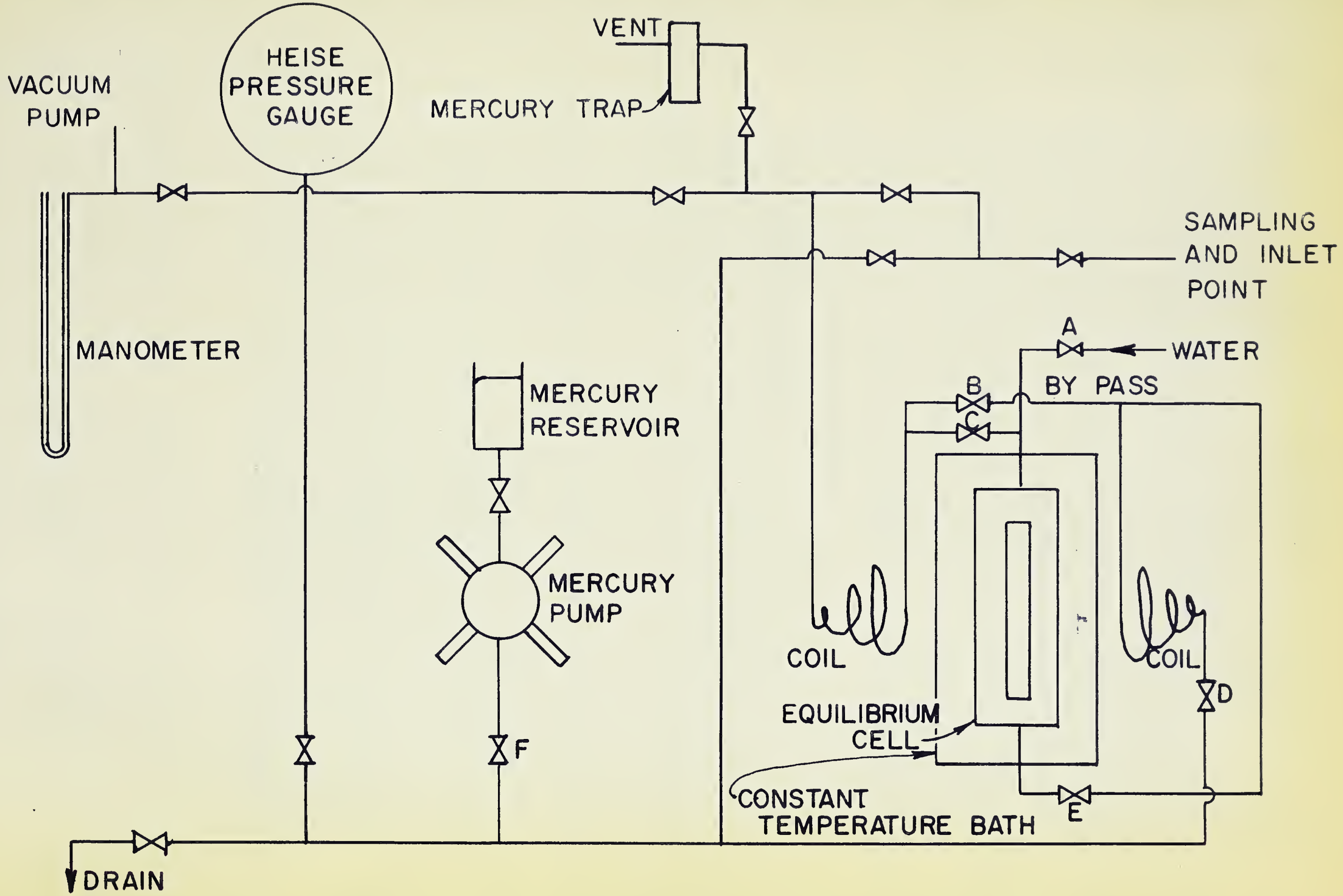

VACUUM PUMP
HEISE PRESSURE GAUGE
VENT
MERCURY TRAP
MANOMETER
SAMPLING AND INLET POINT
A
WATER
B
BY PASS
C
MERCURY RESERVOIR
MERCURY PUMP
COIL
COIL
D
EQUILIBRIUM CELL
F
CONSTANT TEMPERATURE BATH
E
DRAIN

FIGURE 9

SCHEMATIC APPARATUS ASSEMBLY

IV. EXPERIMENTAL

(1) Experimental Apparatus

The system of experimental equipment used was similar to that used at the University of Alberta for other phase equilibria work. The principal unit of the apparatus was the equilibrium cell in which the systems were studied. The equilibrium cell was of the same type used for the above mentioned work and by Katz at the University of Michigan for his investigations of hydrate equilibria.

Figure 9 is a schematic diagram illustrating the general assembly of the basic equipment.

(a) Equilibrium Cell

Investigation of the high pressure phase equilibria involved in a study of gas hydrates requires the use of an equilibrium cell that is built to withstand high pressures and yet will allow one to observe visually the phases present in a system as well as phase reactions between these phases. A cell having these requirements was adapted from a high pressure Jerguson liquid level gauge and is shown in Figure 10. The cell was a high pressure stainless steel chamber fitted with two sight glasses, through which conditions inside the cell could be readily observed. It was capable of withstanding 2,000 lb/in.^{2}abs. at 100°F and had a volume of approximately 120 cc.

The equilibrium cell was enclosed in a clear lucite jacket. The jacket consisted of a 6 inch O.D. lucite cylinder closed at both ends with machined lucite discs. O-rings were used to obtain a tight seal between the discs and the cylinder. The use of O-rings made it easy to remove the discs for dismantling purposes.

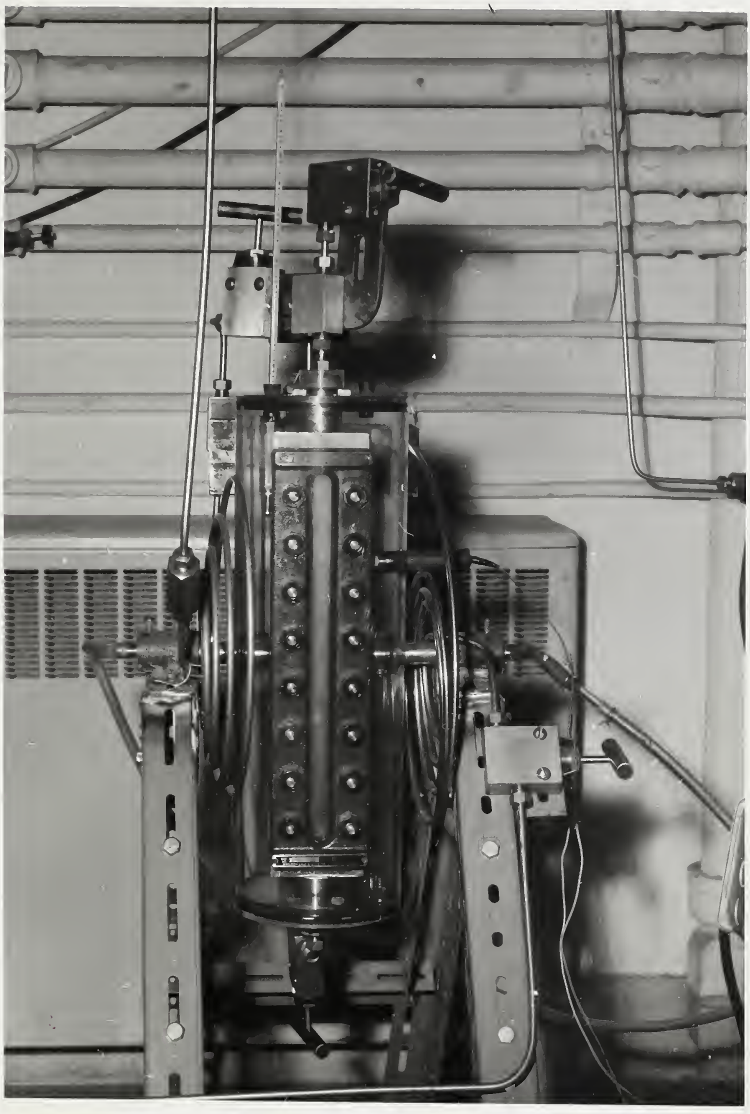


FIG. 10 EQUILIBRIUM CELL

The jacketed equilibrium cell was mounted on a central axis made from two machined rods, each of which was coned at one end. These coned ends fitted into conical seats countersunk in the sides of the equilibrium cell. The other ends of the rods protruded through the sides of the lucite jacket and were fastened to a dexion frame. The weight of the cell was thus transferred to the dexion frame without any strain being put on the lucite jacket. The cell could be rotated about the central axis so that the contents of the cell could be thoroughly and easily agitated. A light was located behind the cell to illuminate the cell interior.

(b) Measurement and Control of Phase Variables

(i) Temperature: The temperature of the equilibrium cell and its contents was controlled by controlling the temperature of varsol, which was circulated from an auxiliary temperature bath through the jacket enclosing the cell. The varsol entered and left the jacket through openings machined in the rods used for the axial mounting.

The auxiliary temperature bath was a small cork insulated tank filled with varsol. An immersion pump mounted in the tank continuously circulated the varsol. The evaporator coil from a Frigidaire refrigerating unit was also mounted in the tank to facilitate cooling of the circulating liquid. A 500 watt immersion heater connected in series with a variac was used for heating purposes. A Minneapolis-Honeywell (15-90°F) refrigeration temperature controller was used to maintain the system at the desired temperatures. The temperature of the bath

could be held constant within ±0.8°F of any set temperature. This kept the temperature within the cell at a constant value within ±0.1°F.

The temperature within the cell was measured with an iron-constantan high-pressure thermocouple assembly which was mounted in the equilibrium cell. This assembly was purchased from the American Instrument Company. A mercury in glass thermometer (0-120°F) was mounted in the temperature bath surrounding the equilibrium cell for the observation of approximate temperatures. A significant temperature lag existed between the outside and inside of the cell. Raising the temperature at the rate of 1°F every 5 minutes would give a lag of 2°F.

(ii) Pressure: Changes of pressure within the equilibrium cell were brought about by injecting mercury into the cell with a hand-operated Ruska mercury pump. The capacity of this pump was 100 cc. and additional mercury was added to the pump from a connecting reservoir as it was needed.

Two Bourdon-tube pressure gauges, manufactured by the Heise Gauge Company, were used for the measurement of pressure. The rating and serial numbers of these gauges were:

(1) No. H 11718 R 0 - 1500 lb/in.^{2}abs.
(2) No. H 3272 R 0 - 5000 lb/in.^{2}abs.

These gauges were calibrated by comparison with a dead weight tester. Each indicated gauge pressure was corrected to absolute pres-

sure by an allowance for atmospheric pressure and for the head of mercury between the gauge and the point in the system at which the pressure was desired.

(c) Assembly of Apparatus

The apparatus was mounted on a dexion framework as shown in Figure 11. All valves, tubing and fittings were Superpressure equipment manufactured by the American Instrument Company, Inc. Valves used were of the 30,000 lb/in.^{2} series and tubing was made of 304 stainless steel having 1/4 inch O.D. and 3/32 inch ID and a pressure rating of 30,000 lb/in.^{2} at 100°F. All connections were union-type Superpressure connections specified by the American Instrument Company, Inc.

A vacuum pump was used to evacuate residual gases from the system and to provide a vacuum source for the sampling operation.

(d) Materials Used

The methane used had a purity of 99.8 mole percent and was supplied by Phillips Petroleum Company. Gas chromatography tests detected a small amount of nitrogen present in the methane. The ethylene was obtained from the Matheson Company, Inc., and was "CP grade", having a minimum purity of 99.5 mole percent. The propylene was obtained from Phillips and had a minimum purity of 99 mole percent. Gas chromatographic analysis showed that there was less than 0.3 mole percent methane present in the propylene. No attempt was made to further purify these gases.

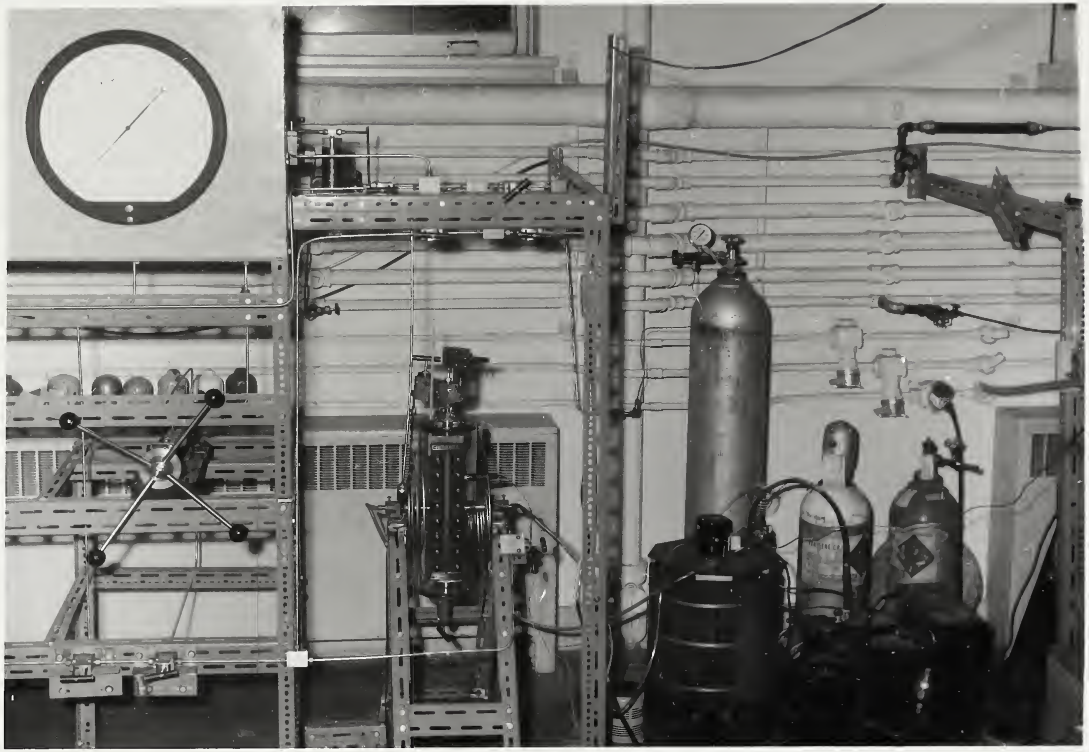


FIG. 11 EXPERIMENTAL APPARATUS

(2) Experimental Technique

(a) Hydrate Formation

The general procedure for forming hydrates was as follows:

(i) The system was first evacuated to remove any residual gases.

(ii) The cell was then filled with mercury and approximately 4 cc of water was drawn into the cell via valve A, (Figure 9) by allowing the mercury to gravitate to the pump with valves E, D and F open.

(iii) The desired gas was then introduced to the cell, through valve C, by utilizing the cylinder pressure of the gas. If two gases were introduced to the cell, the one with the lowest tank pressure was introduced first.

(iv) The contents of the cell were then agitated to insure that the gases were uniformly mixed and that equilibrium existed between the vapor and liquid.

(v) The desired pressure was obtained by increasing or decreasing the level of mercury in the cell by means of the mercury pump.

(vi) The cell contents were then subcooled 5 to 15°F below the temperature at which hydrate formation was anticipated.

(vii) Vigorous agitation of the cell then caused hydrate to form.

(b) Hydrate Equilibria

The hydrate equilibrium points desired are the pressures and temperatures where hydrate just begins to form when a gas of known composition is in the presence of liquid water. For a two component system in three phases there is one degree of freedom, thus the initial

decomposition temperature should be identical to the initial formation temperature at a given pressure. However, for a three component system in three phases, two degrees of freedom exist and the hydrate will melt over a range of temperatures at a given pressure.

The technique for obtaining the pressures and temperatures where hydrates just begin to form for a two component gas in the presence of water was as follows.

After hydrate was formed, the temperature was raised until the hydrate began to melt and the pressure began to rise. The temperature was then raised very slowly until all but a few small crystals of hydrate had melted. The temperature was then reduced a few tenths of a degree and a few small crystals would begin to form on the inside face of the glass windows of the cell. The temperature was then slowly increased again and the pressure and temperature were observed and recorded for the point where these crystals melted. This melting point was quite sharp and thought to be, at least, within 0.5°F of the final melting point.

For the two component systems hydrate was formed and temperatures and their corresponding pressures were observed and recorded for points where the hydrate just began to melt. Some points were also obtained by using the final melting point technique described above. The same results were obtained by using either technique.

(c) Sampling and Analytical Procedure

For the three component systems investigated, samples of the vapor phase were obtained and analyzed for each equilibrium point determined. Sampling of the gas phase was carried out under isobaric conditions by the addition of mercury to the cell at a rate just equal to the rate at which gas was removed. The vapor samples were collected in previously evacuated glass sample bottles.

Equilibrium points, for a particular mixture, were first determined at a high pressure and then, after the vapor sample was removed, the next point was determined at a lower pressure. In this way up to five points, covering the pressure range 2,000 to 100 lb/in.^{2}abs., could be determined for one particular mixture.

The vapor samples were analyzed by using gas phase chromatography. A chromatographic column, packed with "3x" adsorbent, supplied by the Burrell Corporation, was used for the analysis. Calibration curves, which were plots of peak height versus mole percent, were prepared for each of methane, ethylene and propylene. Chromatographic analysis proved to be a fast and accurate method for determining the composition of the vapor phase.

V. EXPERIMENTAL RESULTS

(1) Experimental Phase Equilibrium Data for Binary Systems

(a) Methane-Water System

The hydrate equilibria for the methane-water system have been well defined by a number of investigators. The main purpose of obtaining more equilibrium data in this work was to obtain a check on the experimental technique employed for determining the equilibrium pressures and temperatures for hydrate formation. Comparing the experimental data with data in the literature provided this check.

The pressures and temperatures where hydrate just began to melt were determined for the hydrate, water-rich liquid and vapor equilibrium between 412 lb/in.^{2}abs. and 33°F and 991 lb/in.^{2}abs. and 48.5°F. The data are recorded in Table IV, in the Appendix, and are plotted on Figure 12, along with the published data presented in Table I. The experimental data agree quite well with those of previous investigators. The methane used by Deaton and Frost contained 0.3 percent carbon dioxide and the equilibrium pressures are slightly lower than those obtained in this work and by Villard.

Two points were obtained for the hydrate, ice and vapor equilibrium and they agree with data of Deaton and Frost and Roberts et al. The technique used to obtain these two points was as follows: Hydrate was formed above 32°F and then the system was cooled until ice formed. The pressures and temperatures were

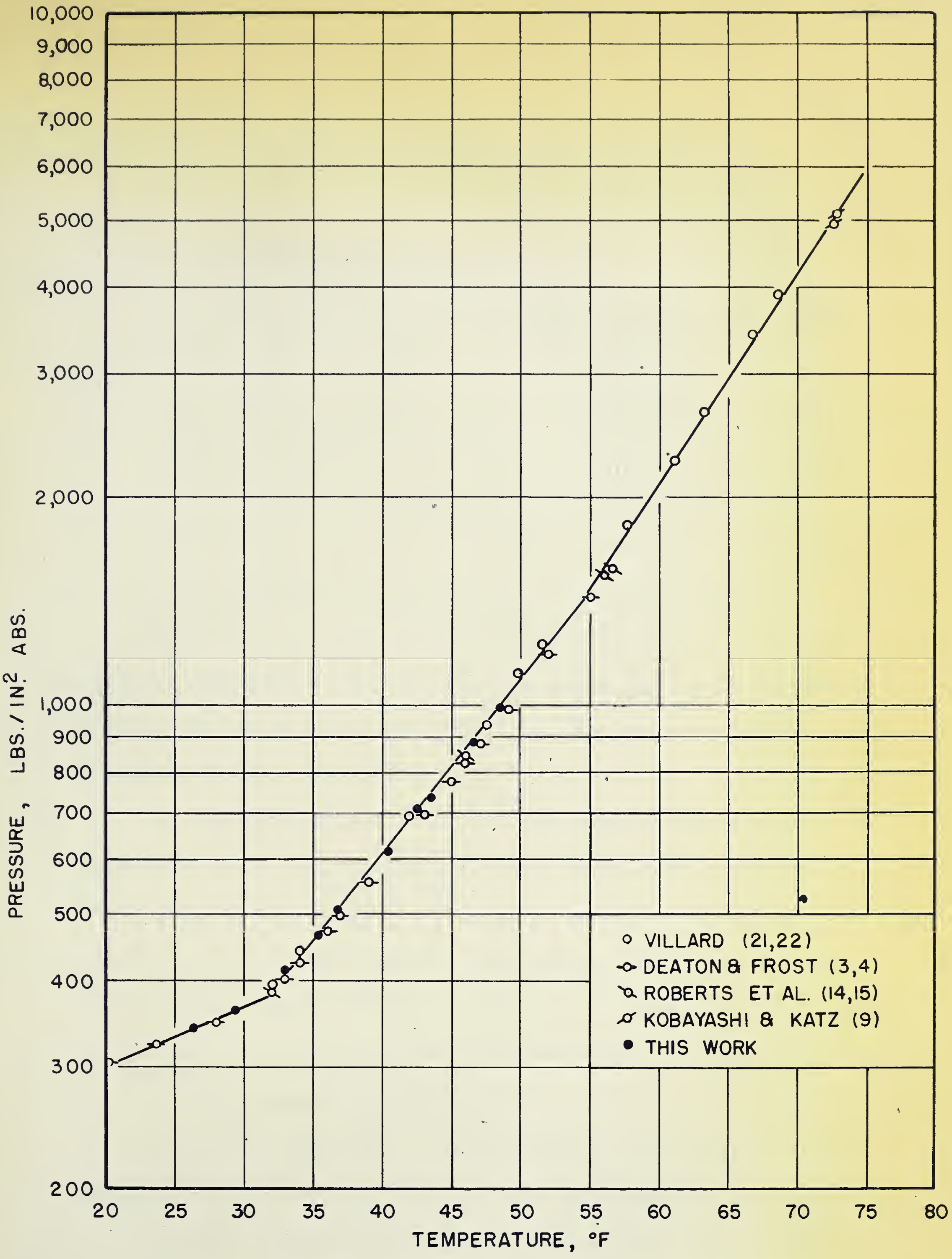


FIG. 12 CONDITIONS FOR HYDRATE FORMATION IN METHANE-WATER SYSTEM

recorded at the instant that the hydrate just began to decompose upon heating.

(b) Ethylene-Water System

The vapor, water-rich liquid and hydrate equilibrium for the ethylene-water system was studied up to 1963 lb/in.^{2}abs. The experimental data are recorded in Table V in the Appendix. The equilibrium pressures and temperatures are plotted on Figure 13, along with the published data presented in Table II. Published data for this equilibrium exists up to 867 lb/in.^{2}abs. The experimental data for pressures below 700 lb/in.^{2}abs. agree very well with those determined by Diepen and Scheffer. The equilibrium pressures published by Villard are a bit higher than those determined in this work and by Diepen and Scheffer. This is particularly noticeable at lower pressures.

In this work, it was found that the slope of the pressure-temperature locus, representing the vapor, water-rich liquid and hydrate equilibrium, begins to increase very rapidly at approximately 700 lb/in.^{2}abs. and 62.9°F. This slope reaches a very high value and then begins to decrease again at approximately 1100 lb/in.^{2}abs. and 64.9°F. The equilibrium temperature at 2000 lb/in.^{2}abs. is 68.3°F.

(c) Propylene-Water System

The vapor, water-rich liquid and hydrate equilibrium for the propylene-water system exists over a very narrow temperature range; 32°F to 34.5°F. Several unsuccessful attempts were made to form

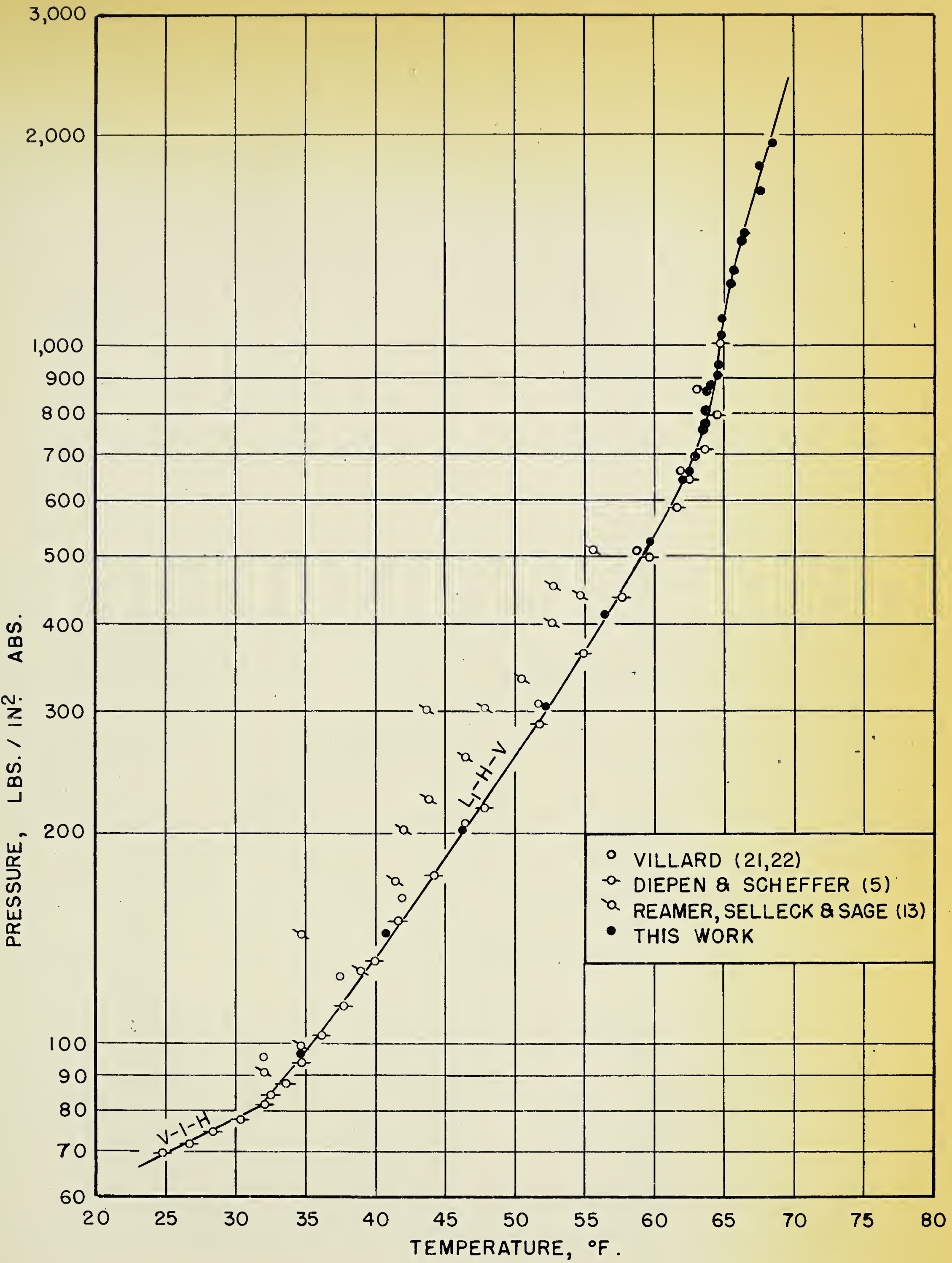


FIG. 13 CONDITIONS FOR HYDRATE FORMATION IN ETHYLENE-WATER SYSTEM.

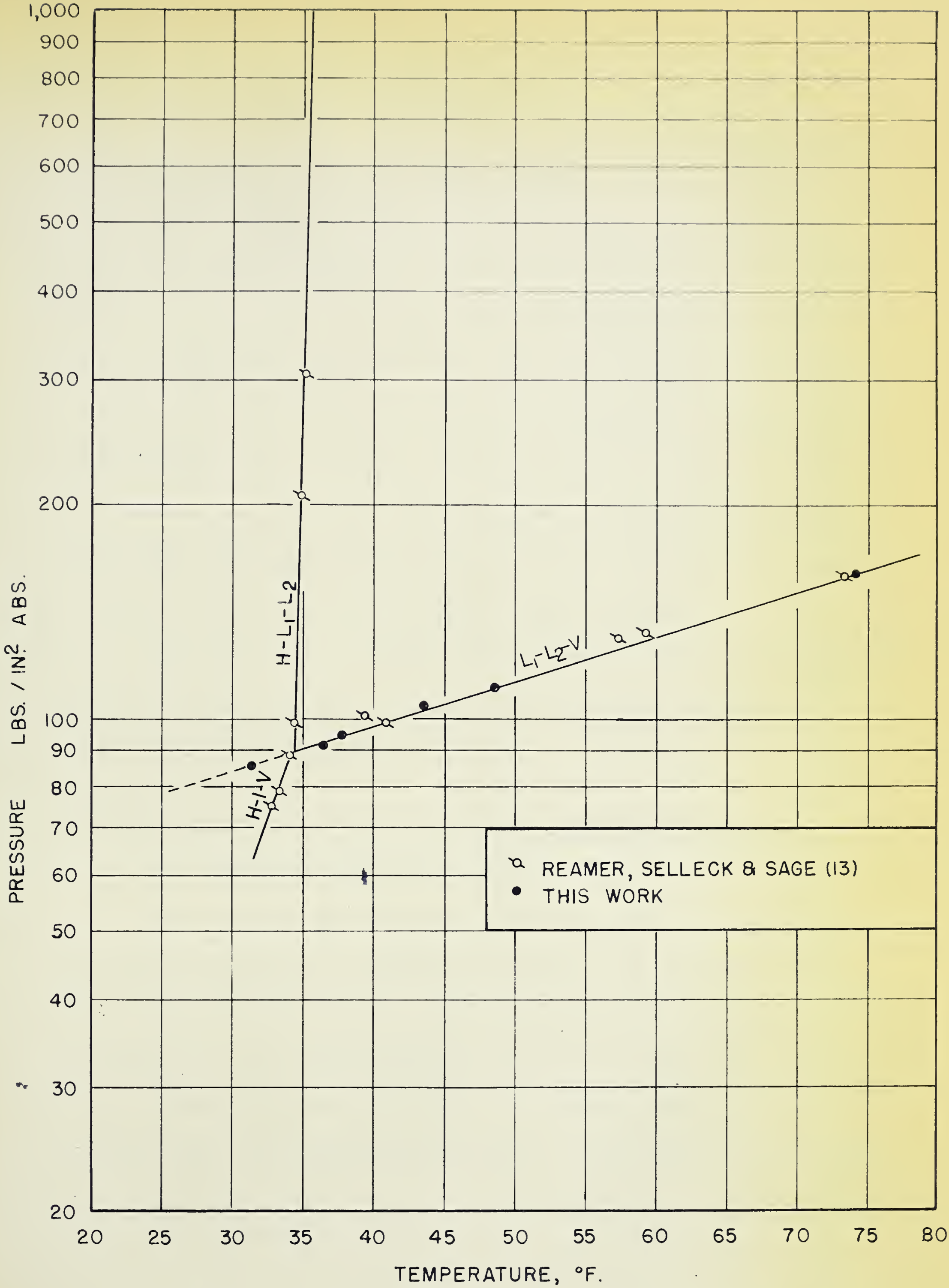


FIG. 14 CONDITIONS FOR HYDRATE FORMATION IN PROPYLENE - WATER SYSTEM.

hydrate in this system. Cooling to 32°F and agitating for a period of several hours failed to produce a hydrate. When the system was subcooled to a temperature below 32°F, ice would form with the result that hydrate formation could not be detected. However, several equilibrium pressures and temperatures were determined for the vapor, water-rich liquid and hydrocarbon-rich liquid equilibrium and these data are recorded in Table VI and plotted on Figure 14. The published data of Reamer, Selleck and Sage from Table III are also plotted on Figure 14. The experimental points for the vapor, water-rich liquid and hydrocarbon-rich liquid equilibrium are seen to agree fairly well with the data of these authors.

From Figure 14 it is seen that the vapor, water-rich liquid, hydrocarbon-rich liquid and hydrate quadruple point exists at approximately 34.5°F and 90 lb/in.^{2}abs.

(2) Experimental Phase Equilibrium Data For Ternary Systems

(a) Methane-Ethylene-Water System

The pressures and temperatures where hydrate just begins to form were determined for mixtures of ethylene and methane at pressures up to 2000 lb/in.^{2}abs. The experimental data are recorded in Table VII in the Appendix and are plotted on Figure 15. The vapor, water-rich liquid and hydrate equilibrium curves for the methane-water and ethylene-water systems are also shown on Figure 15.

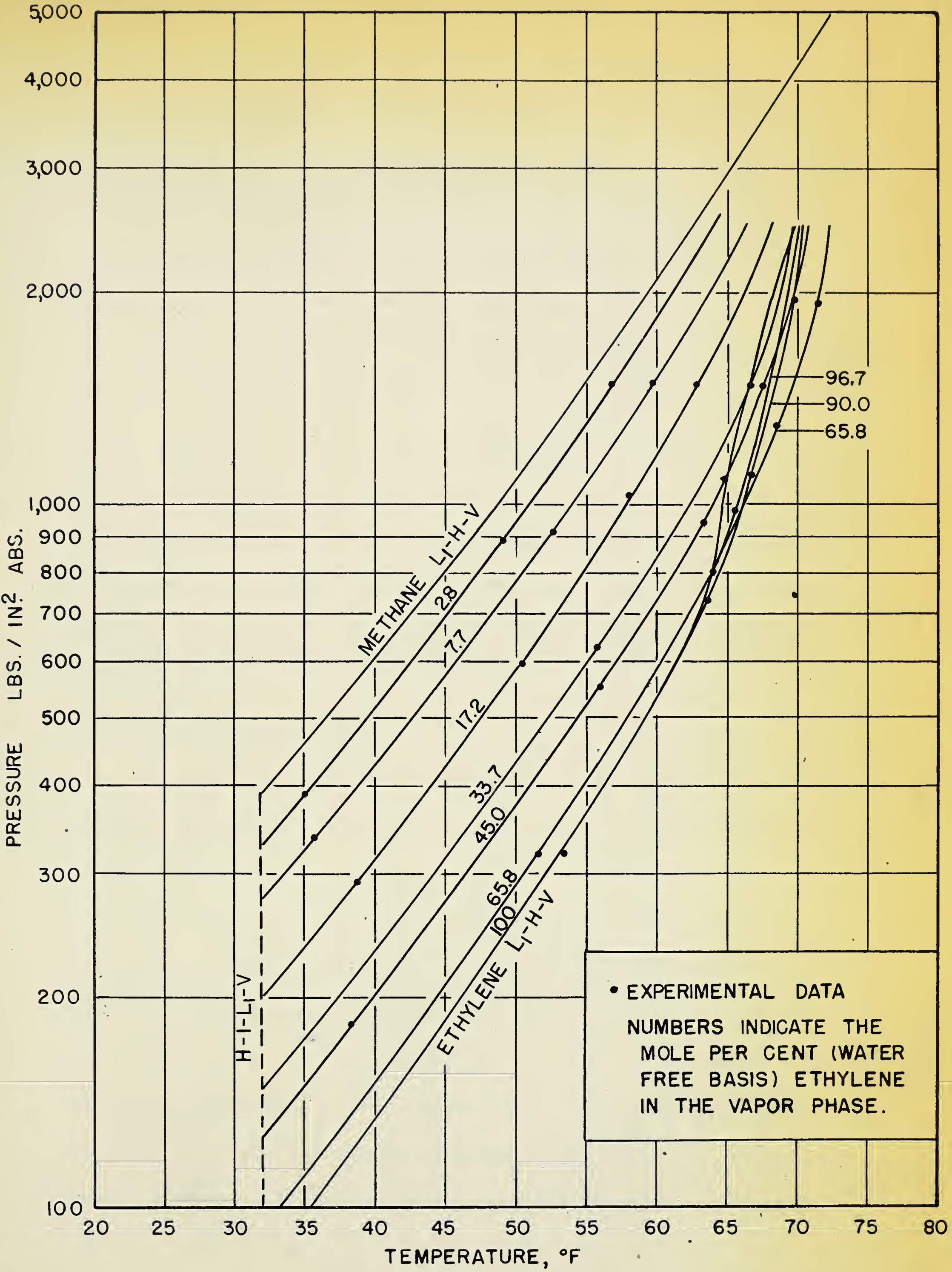


FIG. 15 CONDITIONS FOR HYDRATE FORMATION IN METHANE-ETHYLENE-WATER SYSTEM. (EXPERIMENTAL DATA)

The composition of the vapor phase, on a water-free basis, was determined at each equilibrium point. Curves were drawn through equilibrium points having approximately the same vapor composition and are shown for eight mixtures, ranging in composition from 2.8 mole percent to 96.7 mole percent ethylene.

Below 600 lb/in.^{2}abs., the equilibrium curves all have approximately the same slope and parallel the vapor, water-rich liquid and hydrate equilibrium curves for methane-water and ethylene-water. Above approximately 600 lb/in.^{2}abs., the slopes of these curves begin to increase and this increase becomes more pronounced as the amount of ethylene in the gas increases. Below 730 lb/in.^{2}abs., the equilibrium curves, for compositions greater than approximately 70.0 mole percent ethylene, become indistinguishable from the curve for pure ethylene.

As described previously, the slope of the 100 percent ethylene equilibrium curve becomes much greater at approximately 700 lb/in.^{2}abs. The 65.8 mole percent curve parallels this curve up to 700 lb/in.^{2}abs. and exhibits equilibrium pressures only 15 to 40 pounds higher but does not suddenly increase in slope. It continues as a smooth curve with a gradually increasing slope and crosses the 100 percent curve to give an equilibrium temperature of 71.4°F at 2000 lb/in.^{2}abs. The equilibrium curves for 33.7 and 45.0 mole percent ethylene also cross the 100 percent curve. Hydrate equilibrium curves were determined for mixtures

containing 90.0 and 96.6 mole percent ethylene at pressures greater than 750 lb/in.^{2}abs. Equilibrium pressures for these mixtures are lower than for 100 percent ethylene but are higher than those for the 65.8 percent mixture.

The trend of the equilibrium curves in this region can be more clearly seen on Figure 16, which is a cross plot drawn from Figure 15 and shows constant equilibrium temperature curves on a pressure-composition diagram. For temperatures below 63°F the equilibrium pressure decreases uniformly as the mole percent of ethylene increases. At higher temperatures the pressure decreases uniformly until a composition of approximately 74 mole percent ethylene is reached. However, at higher compositions the curves reverse and the equilibrium pressure increases as the composition increases.

The locus of temperatures and pressures, above which hydrate will not form for mixtures of ethylene and methane, is defined by the curve representing the vapor, water-rich liquid and hydrate equilibrium in the ethylene-water system for pressures up to 700 lb/in.^{2}abs. At higher pressures, it is approximately defined by a smooth extrapolation of this curve up to 950 lb/in.^{2}abs. and by the equilibrium curve for 65.8 mole percent ethylene from 950 to 2000 lb/in.^{2}abs. Only hydrocarbon vapor and water-rich liquid exist to the right of this temperature-pressure locus.

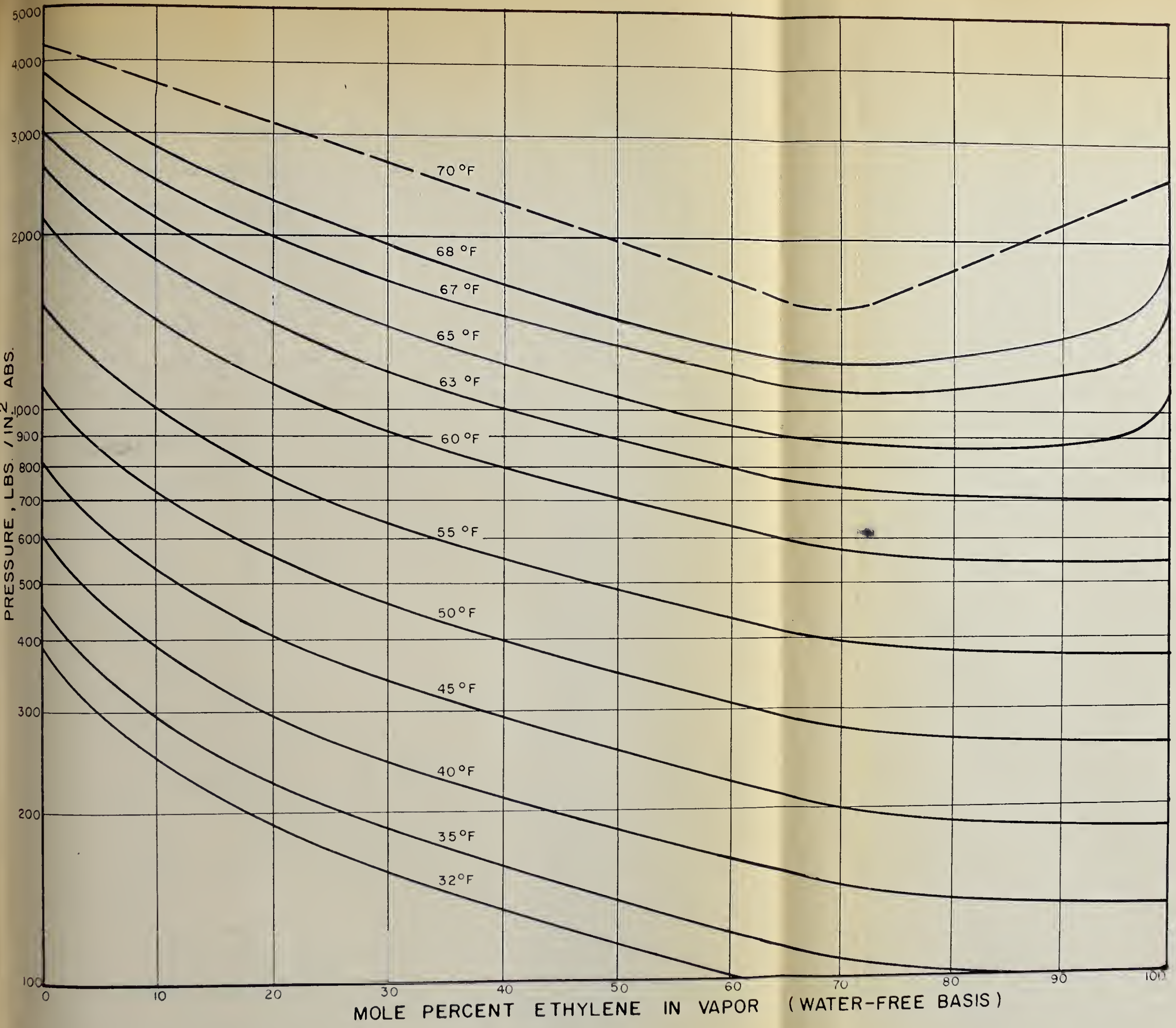


FIGURE 16

HYDRATE FORMATION CONDITIONS FOR METHANE-ETHYLENE MIXTURES

(b) Methane-Propylene-Water System

The conditions of temperature and pressure at which mixtures of methane and propylene will begin to form hydrates in the presence of liquid water are given in Tables VIII and IX in the Appendix and are plotted on Figure 17. Figure 18 is a cross plot of the experimental data.

For gaseous mixtures containing less than approximately 25 mole percent propylene, continuous vapor, water-rich liquid and hydrate equilibrium curves exist which extend to pressures well above 2000 lb/in.^{2}abs. A number of equilibrium points were determined for vapor compositions ranging from 0.5 to 23.9 mole percent propylene (water-free basis) for this equilibrium. Four curves have been drawn to indicate the initial hydrate forming conditions for methane-propylene mixtures of approximately 1.5, 3.0, 10.0 and 15.0 mole percent propylene. These curves have the same characteristic slopes as similar curves for the methane-ethylene-water system.

The addition of small amounts of propylene has a very pronounced effect on the vapor, water-rich liquid and hydrate equilibrium for the methane-water system. The addition of 1.4 mole percent propylene to methane lowers the equilibrium pressure 400 pounds at 50°F.

For mixtures containing greater than 25 mole percent propylene, any vapor, water-rich liquid and hydrate equilibria are terminated by the appearance of a new phase, hydrocarbon-rich liquid. A main

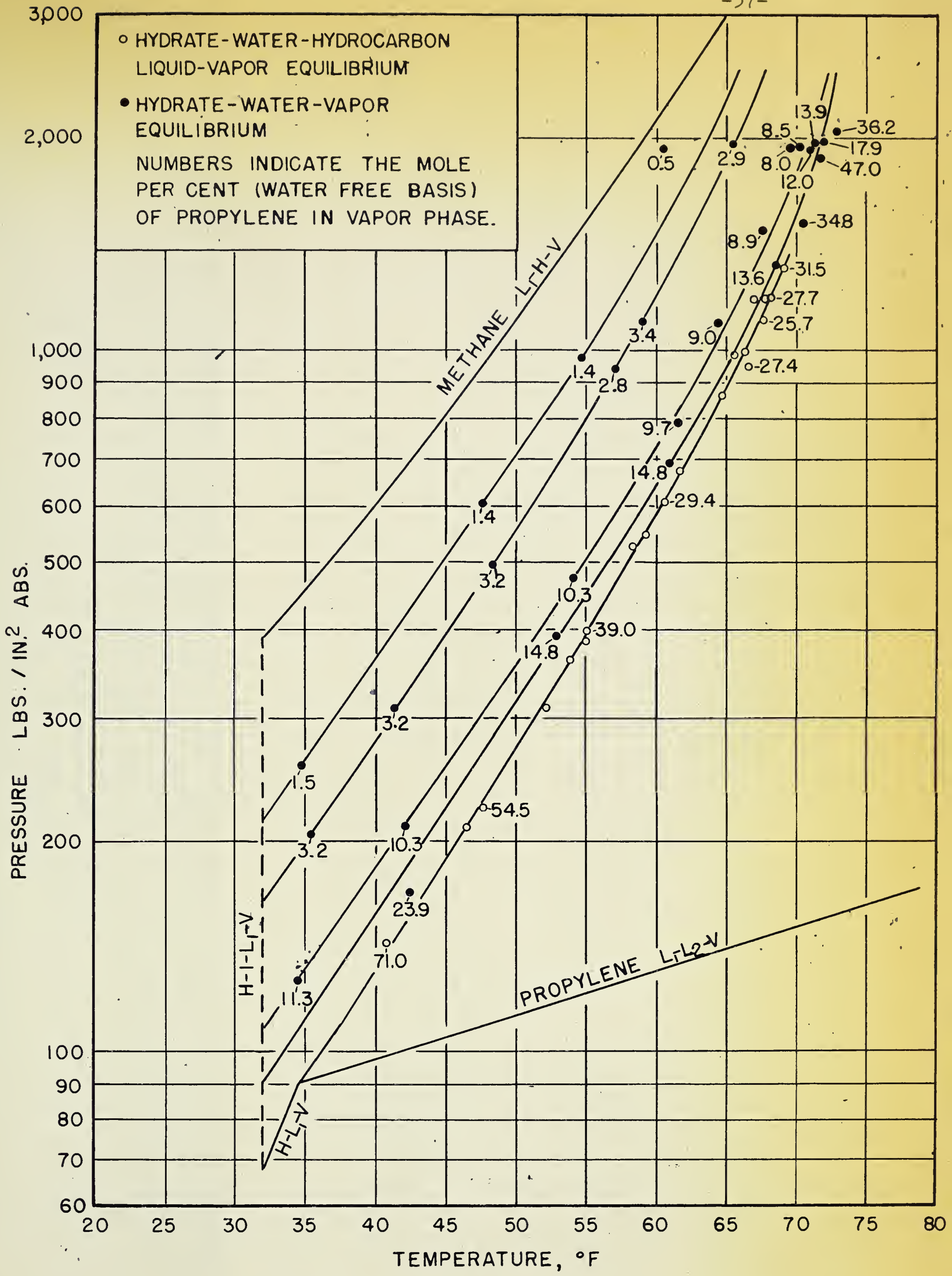


FIG. 17 CONDITIONS FOR HYDRATE FORMATION IN METHANE-PROPYLENE-WATER SYSTEM. (EXPERIMENTAL DATA)

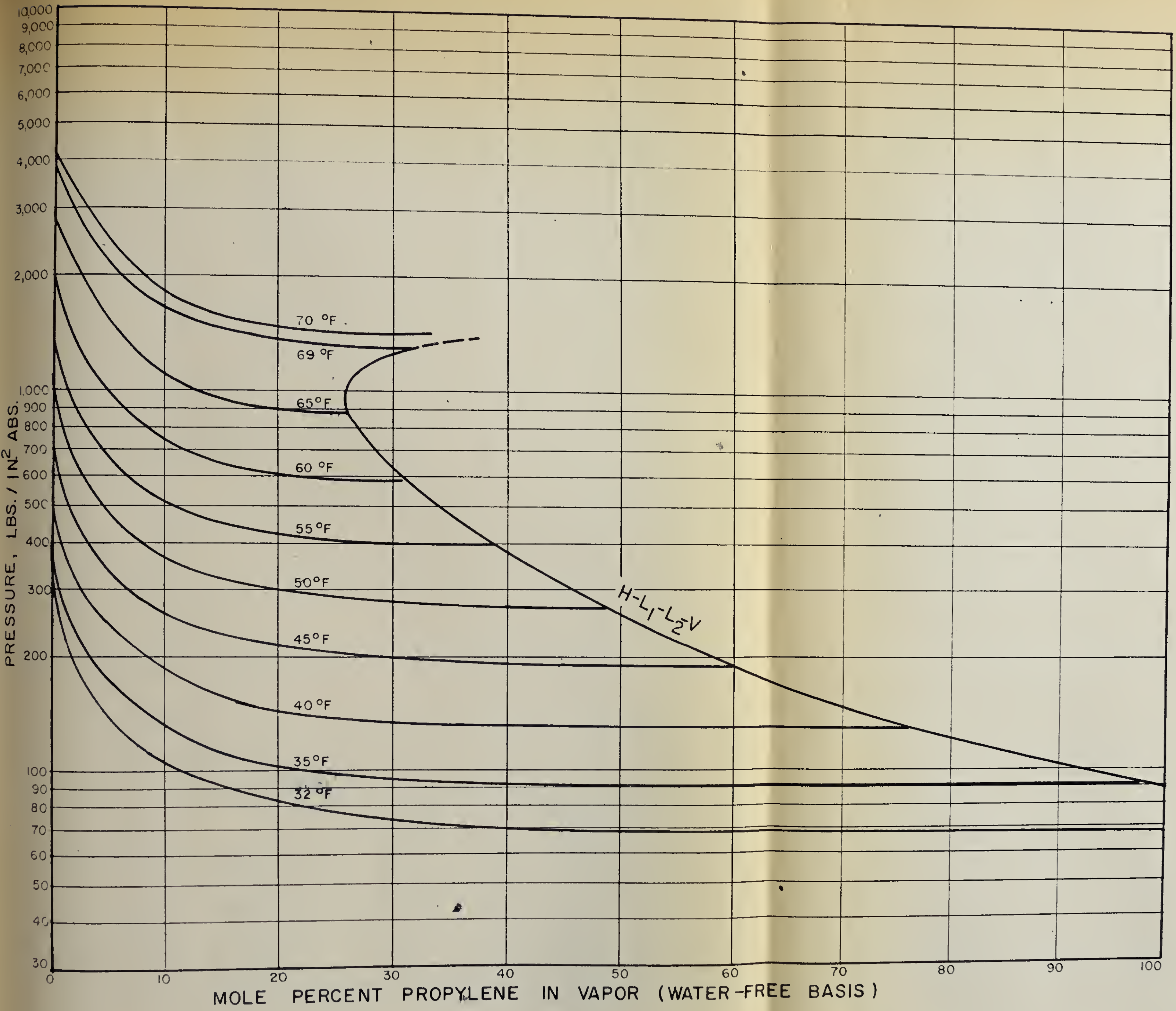


FIG. 18

HYDRATE FORMATION CONDITIONS FOR METHANE-PROPYLENE MIXTURES

point of interest in this system is the appearance of the quadruple locus brought about by the presence of this hydrocarbon liquid. The addition of another component, methane, to the propylene-water system causes the quadruple point (HL_1L_2V) at 34.5°F and 90 lb/in.^{2}abs. to gain a degree of freedom and move out into the three component diagram as a single line having one degree of freedom. Thus, as long as the three phases, vapor, hydrocarbon-rich liquid and water-rich liquid, are present, the conditions of temperature and pressure at which hydrate will form are fixed for any particular vapor composition.

Experimental data were taken to define this quadruple locus. Final melting points and initial melting points were determined and found to fall on the same curve. The composition of the vapor phase was determined at each final melting point. As one progresses to higher pressures along the quadruple locus the amount of hydrocarbon-rich liquid increases and the vapor phase becomes richer in methane. However, near 1000 lb/in.^{2}abs. the mole percent of methane in the vapor reaches a maximum and begins to decrease. This maximum is shown on Figure 18 as 74.5 mole percent methane. Increasing the pressure above 1000 lb/in.^{2}abs. consequently causes the amount of hydrocarbon-rich liquid phase to decrease. The highest point where four phases would exist in equilibrium was found to be 1370 lb/in.^{2}abs. and 69.3°F, when the system was approximately 34.8 mole percent propylene on a water-free basis. At this point, critical phenomena were encountered

and the vapor and hydrocarbon-rich liquid phases appeared to form one phase, thus terminating the four-phase equilibrium.

Initial hydration points were determined for mixtures containing 34.8, 36.2 and 47.0 mole percent propylene respectively, at pressures above 1370 lb/in.^{2}abs. These three points lie on a curve that would result from a smooth extrapolation of the quadruple locus. The hydrocarbon phase for the 47.0 percent mixture was very dense and only a single hydrocarbon phase would exist above approximately 1250 lb/in.^{2}abs. at 70°F. Thus, for mixtures containing greater than approximately 45 mole percent propylene, the region of two hydrocarbon phases terminates below 1370 lb/in.^{2}abs. at the temperatures investigated.

The quadruple locus and a smooth extrapolation of this locus appear to define the temperature-pressure boundary above which hydrate will not form in the methane-propylene-water system.

(3) Hydrate Behavior

The behavior of the hydrates formed in the systems studied was generally the same as that described by other investigators of hydrate equilibria.

As discussed in Section II (3), it was found that at least 5 to 15 degrees of supercooling and vigorous agitation were necessary to first form a hydrate in a particular system. Generally, a greater amount of supercooling was required at higher pressures.

After melting the hydrate phase, sufficient seed crystals would usually remain in the system so that hydrate could be re-

formed by cooling the system to the equilibrium temperature and agitating. Supercooling would speed up the reformation of hydrate but was unnecessary. Seed crystals would remain in the system for an extended period of time, even when the system was left at a temperature and pressure considerably out of the region for hydrate formation.

Once hydration was started in a system crystals would continue to grow quite rapidly and, if the cell contents were not disturbed, the cell would fill up with elongated white crystals which would form on and extend out from the walls of the cell. Continuing agitation of the cell contents after hydration was started, would result in most of the water being converted to hydrate almost immediately. In this case the hydrate would form in a porous like mass somewhat resembling loosely packed ice crystals or snow.

The melting of the hydrate could readily be observed. For the final melting point technique, the few crystals, formed on the walls of the cell, would suddenly melt and little droplets of water would remain. For the initial melting point technique, the point where the hydrate just began to melt could be detected by movements in some part of the hydrate mass. This movement occurred when the crystalline structure of the hydrate mass began to fall apart upon decomposition of the hydrate. The aqueous liquid from the decomposed hydrate could be seen trickling down through the hydrate structure.

When heating a system containing hydrate up to the melting

point, the pressure of the system would slowly increase. The rate of pressure increase would generally increase sharply when the hydrate began to decompose. This provided another method for determining the initial melting point. However, visual observation of the melting points proved to be just as accurate and less painstaking.

(4) Critical Phenomena in CH_4-C_3H_6-H_2O System

The four-phase equilibrium line, representing vapor, hydrocarbon-rich liquid, water-rich liquid and hydrate in equilibrium, was shown to exist to 1370 lb/in.^{2}abs. and 69.3°F, when the system was 34.8 percent propylene and 65.2 percent methane on a water-free basis. At this point interesting critical phenomena were encountered, with the result that the hydrocarbon-rich liquid and vapor became one homogeneous phase. Consequently, the four-phase equilibrium, VHL_1L_2, was terminated. As this point was approached, the surface of demarcation between the hydrocarbon liquid and vapor became fainter and flatter and the liquid phase became more fluid as the surface tension decreased. Finally, only one homogeneous hydrocarbon phase would remain.

When in this region, sudden decreases in pressure would cause a vigorous boiling action to occur and a finely dispersed white fog of varying intensities would form. This fog would sometimes remain for a short time before the single phase would become clear again. Lowering the pressure to 1370 lb/in.^{2}abs. would result in two phases separating out. Agitation near this point would also cause a violent ebullition action to occur.

When this system was cooled to lower temperatures, striking color phenomena occurred at approximately 1382 lb/in.^{2}abs. At a pressure considerably above the region where two hydrocarbon-rich phases existed, the system was colorless. As the pressure was lowered toward this region, the single phase took on a color ranging from yellow to dark red. A further pressure drop of only 1 lb/in.^{2} would cause a phase separation. Opalescence existed over a range of temperatures and the color intensity depended upon the temperature. The color was fairly intense at 55.7°F and 1382 lb/in.^{2}abs. but was even more intense at 49.3°F and 1382 lb/in.^{2}abs. A maximum intensity of color would be expected to occur at the critical point, thus indicating, that the critical point for the hydrocarbon rich phases, in the 34.8 mole percent propylene mixture, existed at a temperature and pressure close to 49.3°F and 1382 lb/in.^{2}abs.

(5) Correlation of Experimental Data

The desired correlation of the experimental data is a method of predicting the effect that propylene and ethylene will have on the hydrate forming conditions for a gas mixture containing either or both of these components. As described in Section III (5), vapor-solid equilibrium ratios have proven fairly successful for predicting conditions for hydrate formation in natural gases. From the experimental data obtained for the methane-propylene-water and methane-ethylene-water systems, it was possible to calculate vapor-solid equilibrium ratios for ethylene and propylene. That is,

the vapor phase analysis at hydrate equilibrium points in these systems and the vapor-solid equilibrium ratios for methane shown in Figure 8 were used, along with the relationship $\Sigma \frac{y}{K_{VS}}$ must equal unity at conditions of hydrate formation, to calculate vapor-solid equilibrium ratios for ethylene and propylene. Vapor phase compositions were taken from Figures 16 and 18, which were used to expand and extrapolate the experimental data. The calculated equilibrium ratios are given in Tables X and XI. Smoothed curves representing these equilibrium ratios are plotted on Figures 19 and 20.

The constant pressure curves, for the solid-vapor equilibrium ratios for ethylene, have a gradually decreasing slope until a value for K_{VS} of approximately 0.8 is reached. The slope then increases quite sharply. This occurs because methane-ethylene mixtures containing greater than about 70 percent ethylene form hydrates at essentially the same conditions as for pure ethylene. The equilibrium ratios are equal to unity at the pressures and temperatures at which pure ethylene forms hydrate. The curves for pressures of 1000 lb/in.^{2}abs. and higher, exhibit a temperature maximum above values of K_{VS} equal to 0.9 because of the nonuniformity of arrangement exhibited by the constant composition equilibria curves in the region above 700 lb/in.^{2}abs. and 62.9°F (Figure 15). The curves for pressures of 1500 lb/in.^{2}abs. and higher have a much smaller slope than the other curves. This is mainly because the values of K_{VS} for methane are almost equal to unity at these pressures and have approximately the same value at different temperatures.

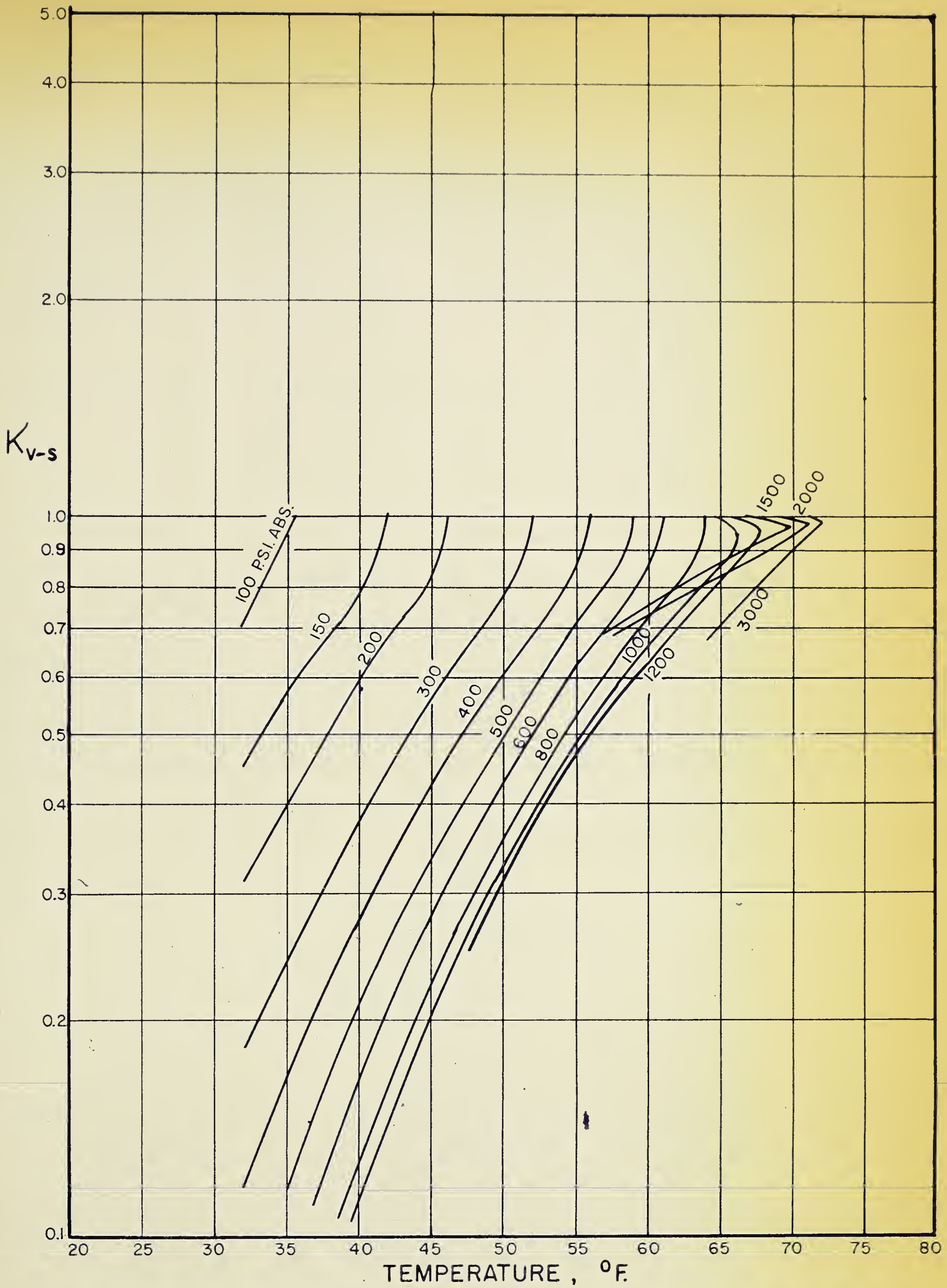


FIG. 19

SOLID-VAPOR EQUILIBRIUM RATIOS FOR ETHYLENE

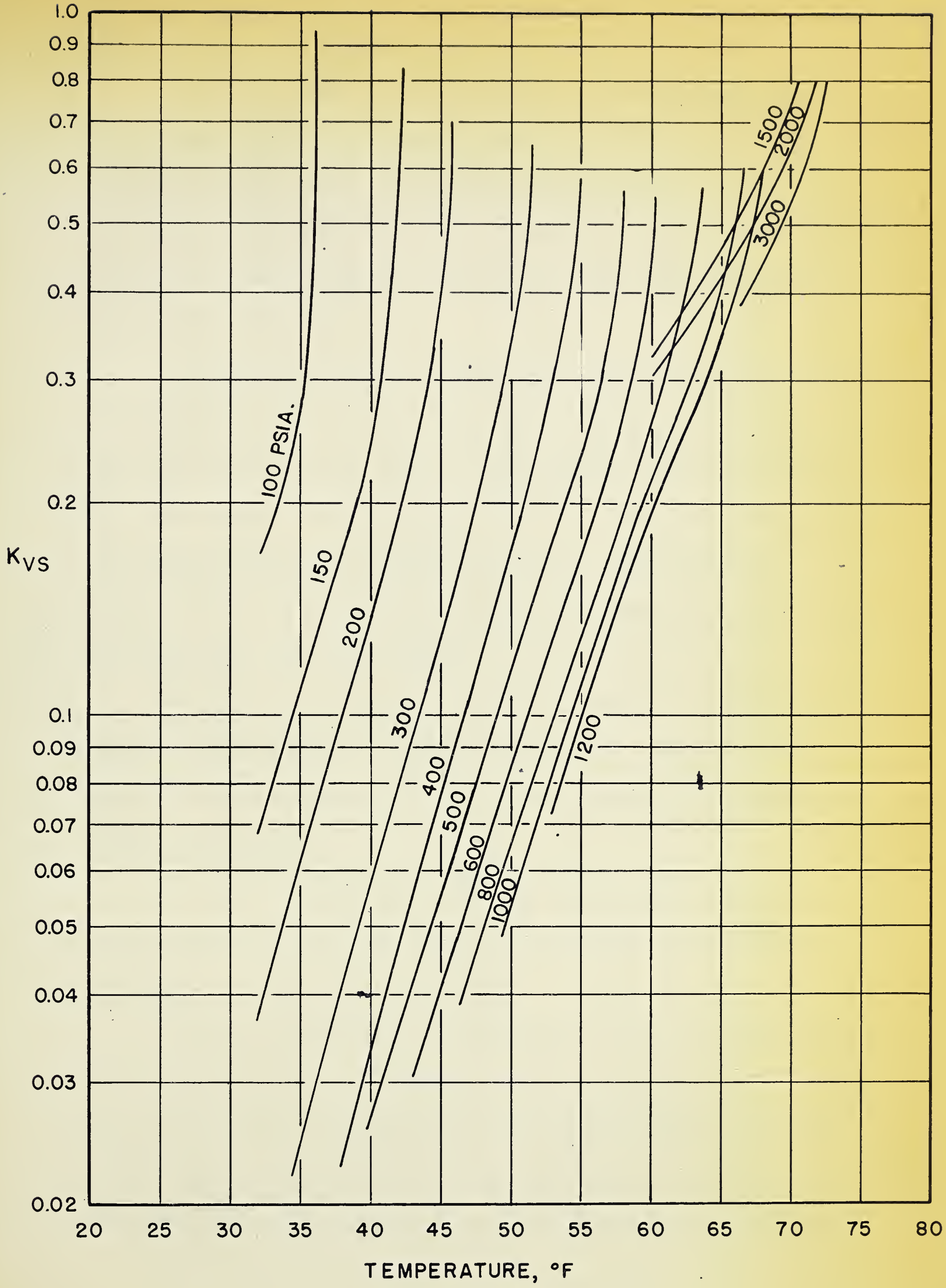


FIG. 20 SOLID-VAPOR EQUILIBRIUM RATIOS FOR PROPYLENE.

The solid-vapor equilibrium curves for ethane (1), which forms hydrate at nearly the same conditions as ethylene, have somewhat the same slope as the curves for ethylene. However, the value of the equilibrium ratio at any particular temperature and pressure is smaller than the value at the same temperature and pressure for ethylene.

The constant pressure, solid-vapor equilibrium ratio curves for propylene, shown on Figure 20, have a gradually increasing slope and become very steep at values of K_{VS} greater than approximately 0.3. The highest value of K_{VS} calculated at each pressure, is the value where four-phase equilibrium exists at this pressure. Curves for 1500 lb/in.^{2}abs. and higher pressures, again have different slopes than the other curves.

Constant pressure equilibrium ratio curves for propane (1) exhibit slopes similar to those for propylene. This is to be expected, since a quadruple locus is also present in the methane-propane-water system.

To use the equilibrium constants to calculate hydrate forming conditions for some temperature, pressures are assumed until $\sum \frac{y}{K} = 1$ for all the components.

In order to evaluate the usefulness of the calculated vapor-solid equilibrium ratios, hydrate forming conditions were calculated for a gas mixture containing 64.8 mole percent methane, 31.7 mole percent ethylene and 3.5 mole percent propylene. These predicted conditions were then compared with experimental equilibrium temper-

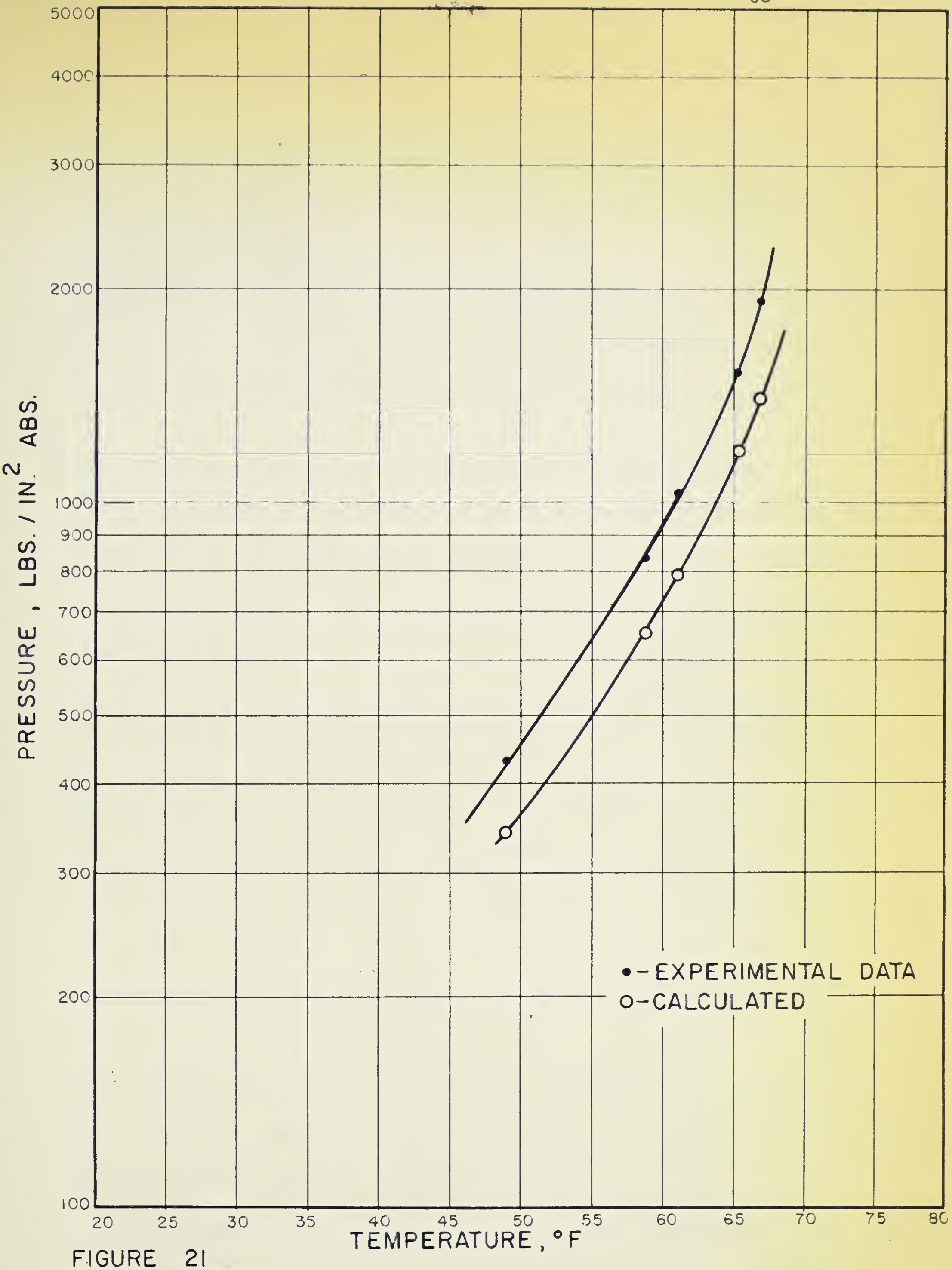


FIGURE 21

COMPARISON OF CALCULATED WITH EXPERIMENTAL CONDITIONS FOR HYDRATE FORMATION

GAS COMPOSITION: 64.8 MOLE % CH_4
31.7 MOLE % C_2H_4
3.5 MOLE % C_3H_6

atures and pressures, which were determined for a mixture of the same composition. The comparison of the calculated and experimental hydrate forming conditions is shown on Figure 21 and given in Table XII in the Appendix. It is seen that the predicted equilibrium pressure at any given temperature is much lower than the experimental value. In fact, the predicted values are from 21 to 28 percent in error.

(6) Phase Diagrams for the Methane-Propylene-Water System

In general, the variations in concentration of three component systems are conveniently expressed by means of isobaric, isothermal triangular diagrams. Sufficient phase composition data were not obtained to be able to construct quantitative diagrams of this type for the methane-propylene-water system. However, sufficient information was available to draw, schematically, the temperature composition diagrams which make up the boundaries of constant pressure space figures for this system. These were drawn for pressures of 450 lb/in.^{2}abs. and 1500 lb/in.^{2}abs. and are shown in Figures 22 and 24. Using these figures as guides, schematic constant temperature sections have been drawn, which we thought to be representative of the types of diagrams that could be drawn, if the necessary phase composition data were available. Although these diagrams are only schematic, they are an aide to a better understanding of the phase relations peculiar to this system.

The pressures of 450 lb/in.^{2}abs. and 1500 lb/in.^{2}abs. have been selected for illustration in order to present the features which give rise to the four-phase equilibrium, VL_1L_2H, and the features

which cause this equilibrium to be terminated. A quadruple point exists at 450 lb/in.^{2}abs. and 56.6°F. At 1500 lb/in.^{2}abs. we are above the VL_1L_2 region so that the four-phase equilibrium will not exist at this pressure.

The boundary of the space figure for 450 lb/in.^{2}abs. is shown in Figure 22 and for 1500 lb/in.^{2}abs. in Figure 24. The temperatures of triple points for the methane-water system were obtained from Figure 13 and for the propylene-water system from Figure 14. Boiling points and freezing points for the pure substances are readily available. Where temperatures of important features had not been determined experimentally, they could be estimated with sufficient accuracy.

The constant temperature sections drawn at 450 lb/in.^{2}abs. are shown in Figure 23. The quadruple point is an equilibrium between L_1L_2V and H and is at 56.6°F. Associated with this point will be four three-phase equilibria, VL_1L_2, VL_2H, HL_1V and HL_2L_1. Since the three-phase equilibrium, L_2L_1V, is the only one starting at a higher temperature than the quadruple point, we know the four-phase equilibrium will be formed by one triangle coming down and three going away from the quadruple temperature.

Figure 23(b) is typical of diagrams for this system at 450 lb/in.^{2}abs., when the temperature is greater than 56.6°F but less than approximately 150°F. The L_2L_1V equilibrium is represented by a triangle having the phases mentioned at its vertices. Associated with this three-phase area there must be three two-phase regions and three one-phase regions. From the methane-water edge of the

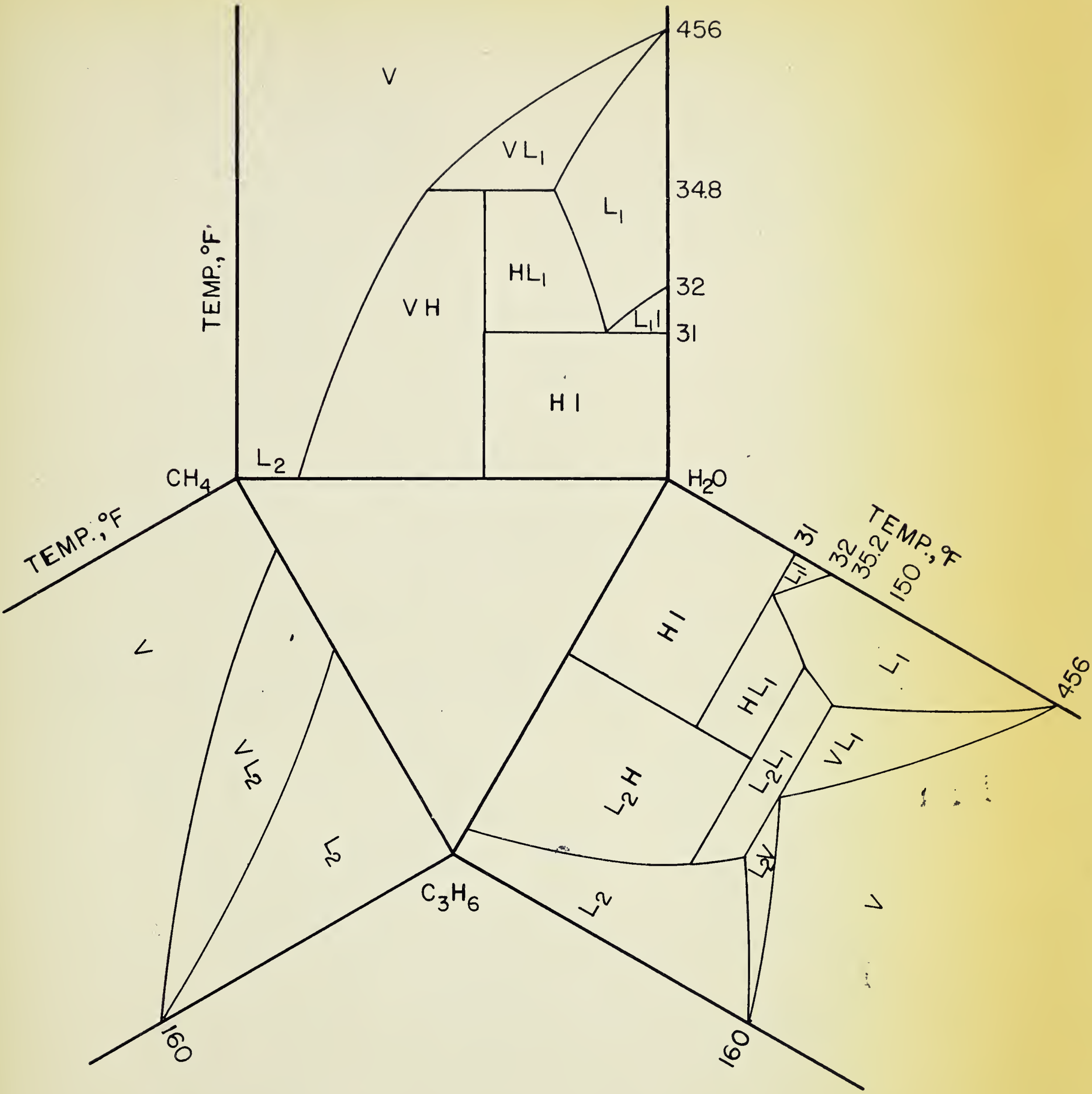
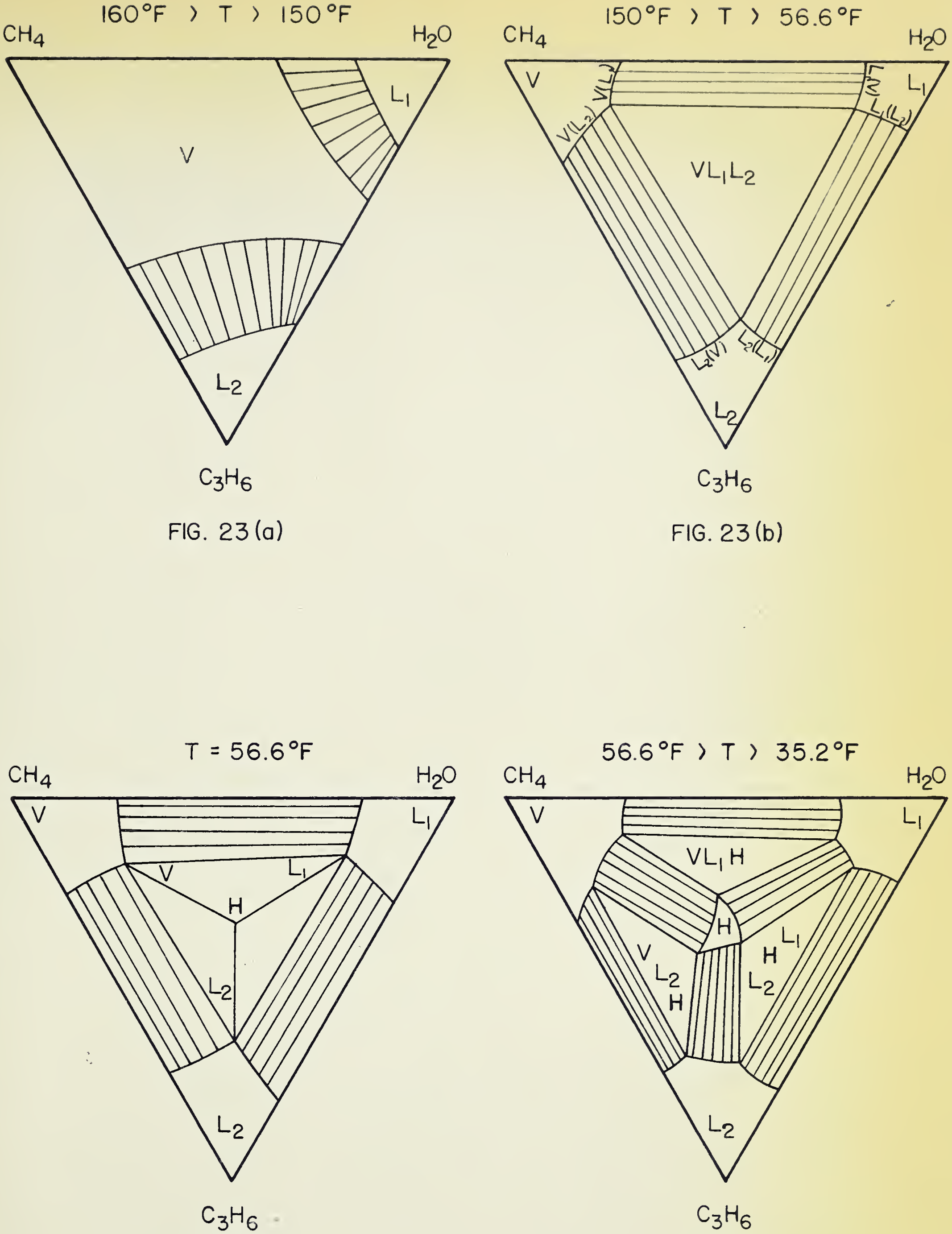

TEMP., °F
V
VL$_1$
L$_1$
HL$_1$
VH
L$_1$I
HI
L$_2$
456
34.8
32
31
CH$_4$
H$_2$O
C$_3$H$_6$
TEMP., °F
TEMP., °F
31
32
35.2
150
456
160
160
V
VL$_2$
L$_2$
HI
L$_1$I
L$_1$
HL$_1$
VL$_1$
L$_2$L$_1$
L$_2$H
L$_2$V
L$_2$
V

FIG. 22 BOUNDARY OF SPACE DIAGRAM FOR METHANE-PROPYLENE-WATER SYSTEM AT 450 POUNDS PER SQUARE INCH ABSOLUTE.



CH_4
H_2O
C_3H_6
V
L_1
L_2
V
V(L$_1$)
V(L$_2$)
L_1(V)
$L_1(L_2)$
VL_1L_2
L_2(V)
$L_2(L_1)$
V
L_1
H
L_2
VL_1 H
H
V
L_2
H
H
L_1
L_2

160°F ⟩ T ⟩ 150°F

FIG. 23 (a)

150°F ⟩ T ⟩ 56.6°F

FIG. 23 (b)

T = 56.6°F

FIG. 23 (c)

56.6°F ⟩ T ⟩ 35.2°F

FIG. 23 (d)

FIG. 23 SCHEMATIC CONSTANT TEMPERATURE SECTIONS FOR METHANE-PROPYLENE-WATER SYSTEM AT 450 POUNDS PER SQUARE INCH ABSOLUTE.

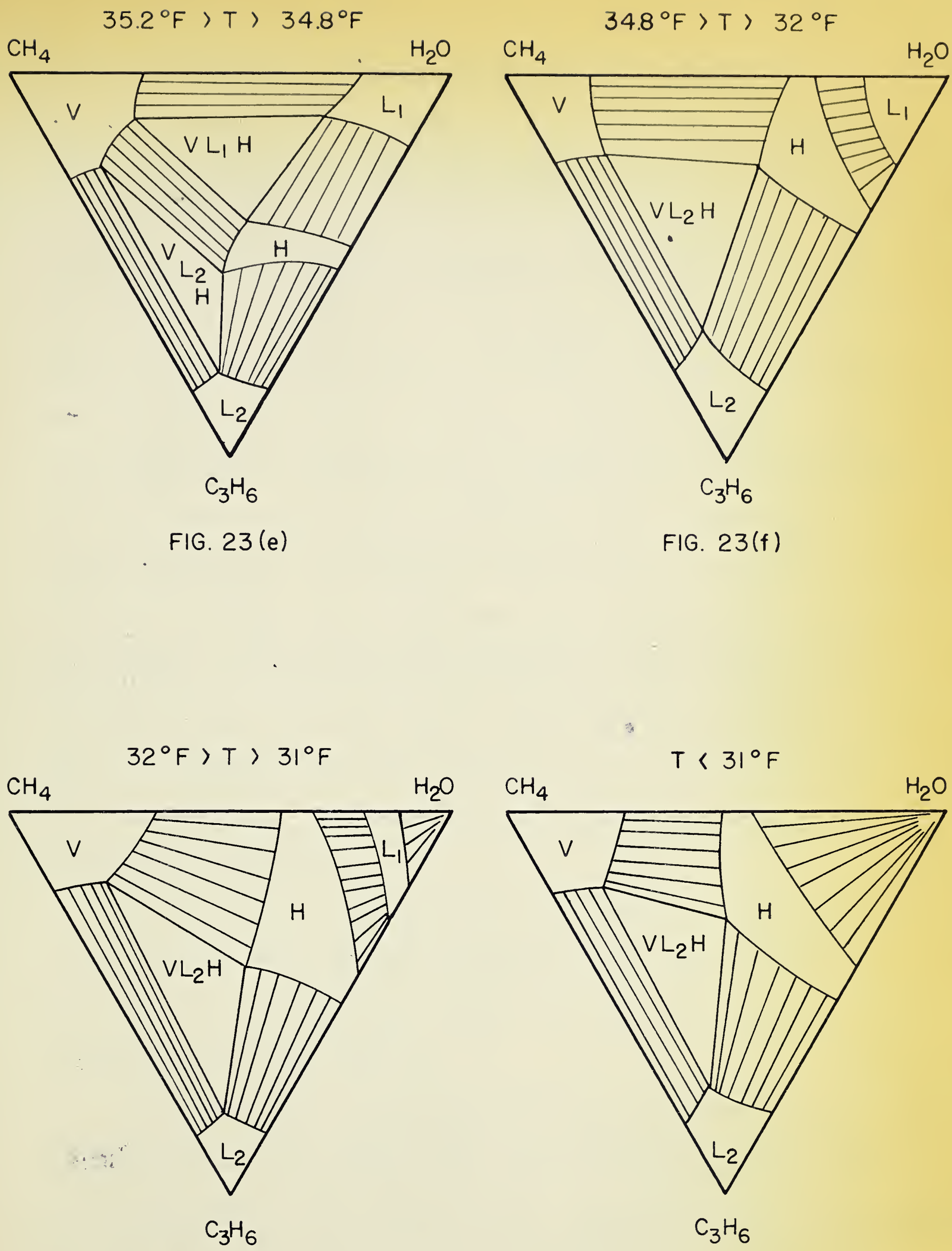

35.2 °F > T > 34.8 °F
CH4
H2O
V
L1
V L1 H
V L2 H
H
L2
C3H6
34.8 °F > T > 32 °F
CH4
H2O
V
L1
H
V L2 H
L2
C3H6
32 °F > T > 31 °F
CH4
H2O
V
L1
H
V L2 H
L2
C3H6
T < 31 °F
CH4
H2O
V
H
V L2 H
L2
C3H6

FIG. 23 (e)

FIG. 23 (f)

FIG. 23 (g)

FIG. 23 (h)

FIG. 23 (CON'T.) SCHEMATIC CONSTANT TEMPERATURE SECTIONS FOR METHANE-PROPYLENE-WATER SYSTEM AT 450 POUNDS PER SQUARE INCH ABSOLUTE.

figure, lines representing V in equilibrium with L_1 and L_1 in equilibrium with V will be generated. Similarly, from the propylene-water edge, lines representing L_2 in equilibrium with L_1 and L_1 in equilibrium with L_2 will be generated and lines representing V in equilibrium with L_2 and L_2 in equilibrium with V will be generated from the methane-propylene edge of the diagram. These lines will all be terminated by the addition of a phase. For example, the line representing L_2 in equilibrium with L_1 -- designated $L_2(L_1)$ -- will be terminated by the appearance of V. Coming down from the propylene-water eutectic at approximately 150°F there will be three space curves representing V in equilibrium with L_2 and L_1 -- $V(L_2L_1)$, $L_2(L_1V)$ and $L_1(VL_2)$. These curves will pierce the constant temperature plane at points which will be vertices of the triangle representing the three phase area L_2L_1V. Any point within this three-phase area represents the total composition of a system containing these three phases. The composition of the phases are given by the vertices of the triangle.

At temperatures below 56.6°F but above 35.2°F we can expect to find three three-phase areas representing L_2VH, L_1VH and HL_1L_1. These areas are shown on Figure 23 (d) along with the associated two-phase and one-phase regions.

At 56.6°F, which is the quadruple temperature, we find the four three-phases areas, VL_1H, VL_1L_2, VL_2H and HL_1L_2, combining into one four-phase area, which represents the VL_1L_2H equilibrium (Figure 23(c)). Each one of the four vertices in this four-phase area represents the fixed composition of one of the phases.

At 35.2°F, we are at the HL_1L_2 equilibrium for the propylene-water system and, as shown on Figure 23 (e), this equilibrium does not exist below this temperature for the three component system. Similarly the HLV equilibrium does not exist below 34.8°F, which is the temperature for this equilibrium in the methane-water system. This is shown on Figure 23 (f). At 32°F ice will begin to form and an L_1I equilibrium exists (Figure 23 (g)). Below about 31°F no L_1 is present and an equilibrium between hydrate and ice exists (Figure 23 (h)). Figure 23 (a) is representative of diagrams for this system at temperatures approximately between 150 and 160°F, at 450 lb/in.^{2}abs.

At 1500 lb/in.^{2}abs. we are above the critical locus and no hydrocarbon-rich liquid will form. The boundary of the three dimensional space figure at this pressure is shown in Figure 24 and constant temperature sections are shown in Figure 25.

Above approximately 70.5°F, at this pressure, a hydrate phase is not present and only water-rich liquid and a hydrocarbon-rich phase will exist. This hydrocarbon phase is designated both by the symbol (L_2) and (V) to indicate that the density of the phase changes with composition.

Below 70.5°F, a hydrate phase appears and $H(V)L_1$ and $H(L_2)L_1$ equilibria are present. These three-phase areas are shown on Figure 25 (a) which is similar to Figure 23 (d) except that the VHL_2 and VL_2 equilibria do not exist. The $H(V)L_1$ equilibrium terminates at 54.7°F, which is the temperature for this equilibrium in the

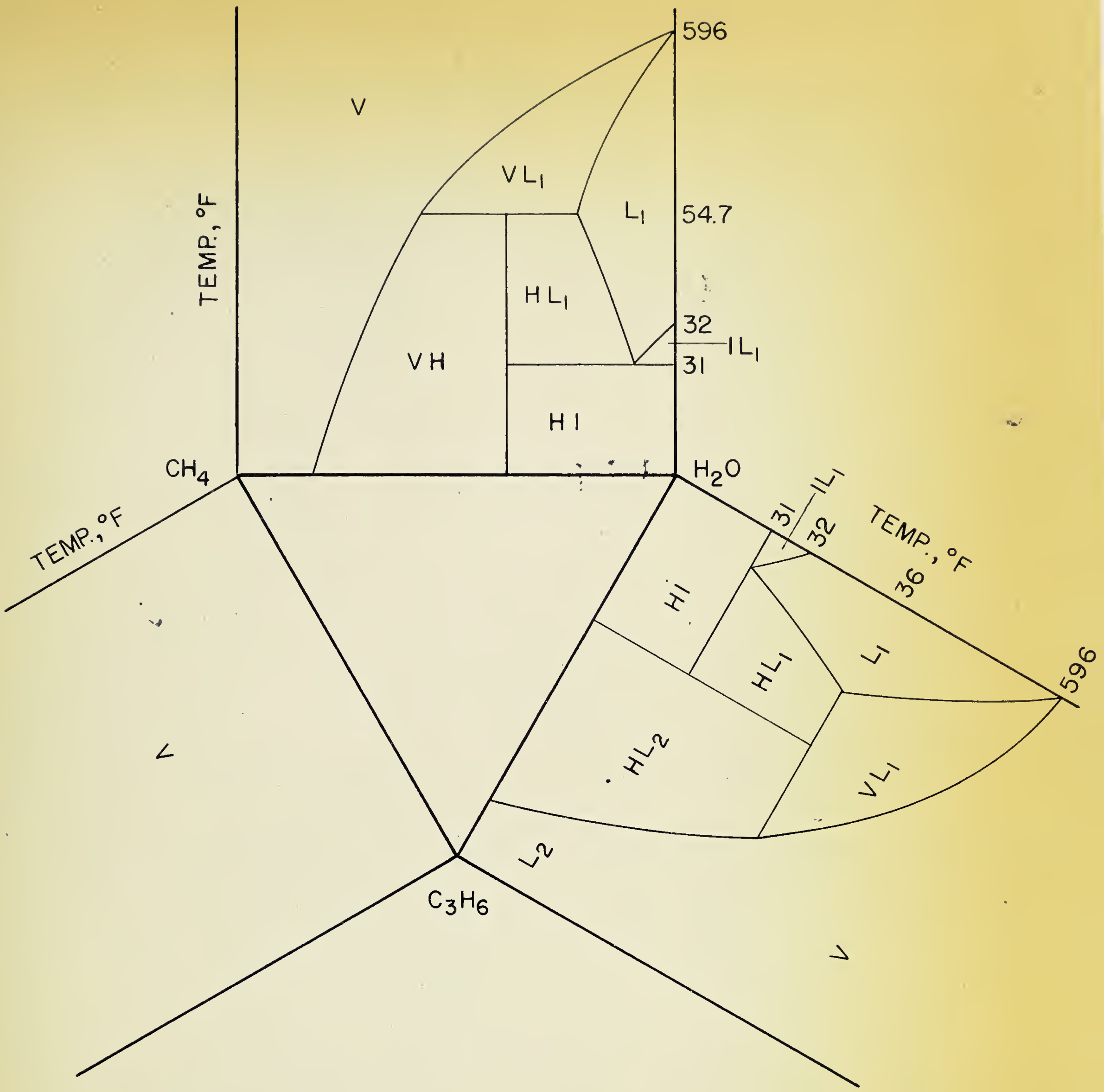

596
V
VL_1
L_1
54.7
TEMP., °F
HL_1
32
IL_1
31
VH
HI
CH_4
H_2O
TEMP., °F
31
IL_1
32
TEMP., °F
36
HI
HL_1
L_1
596
HL_2
VL_1
V
L_2
C_3H_6
V

FIG. 24 BOUNDARY OF SPACE DIAGRAM FOR METHANE – PROPYLENE – WATER SYSTEM AT 1500 POUNDS PER SQUARE INCH ABSOLUTE.

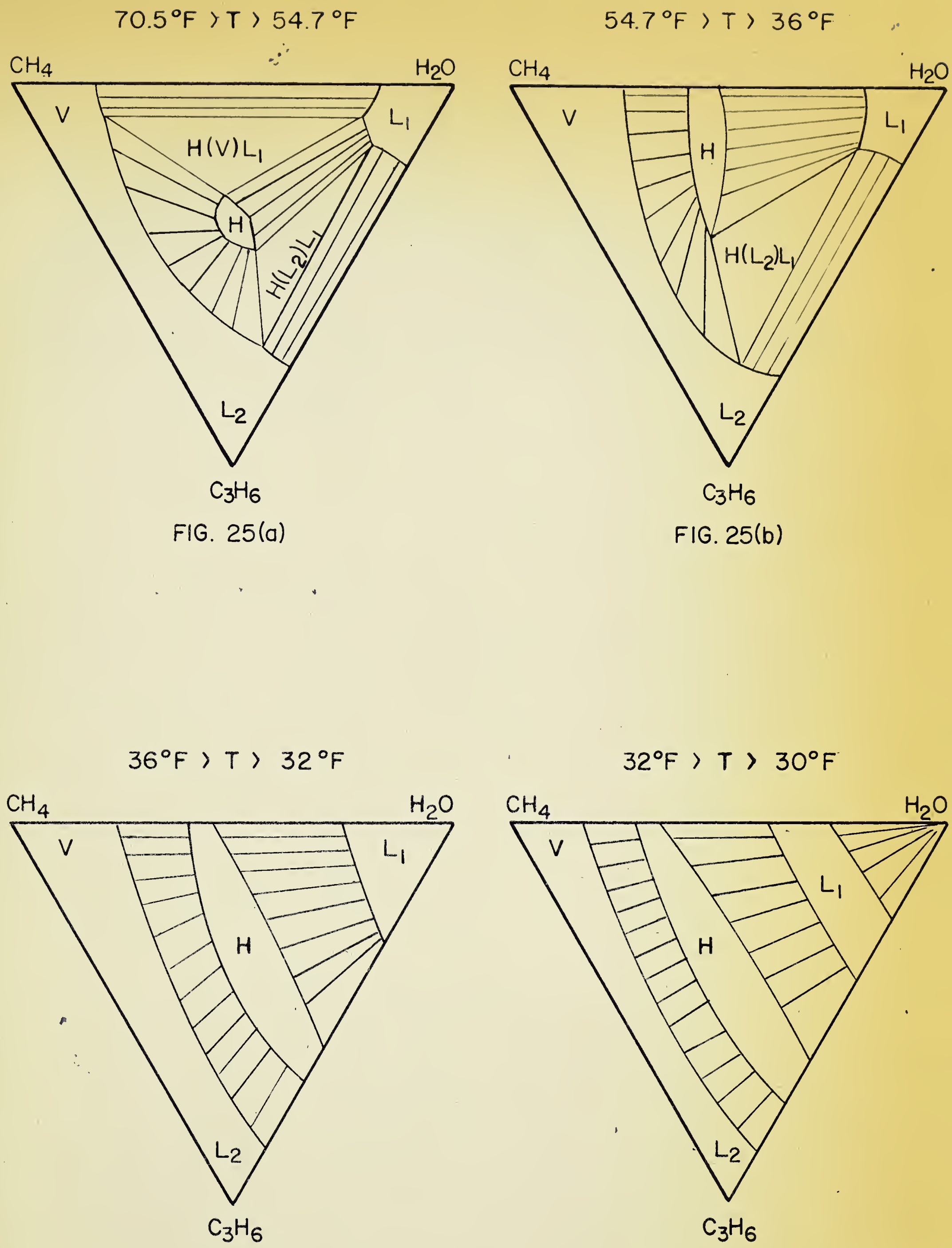

70.5°F > T > 54.7°F
54.7°F > T > 36°F
CH4
H2O
C3H6
V
L1
L2
H
H(V)L1
H(L2)L1
36°F > T > 32°F
32°F > T > 30°F

FIG. 25(a)

FIG. 25(b)

FIG. 25(c)

FIG. 25(d)

FIG. 25 SCHEMATIC CONSTANT TEMPERATURE SECTIONS FOR METHANE – PROPYLENE – WATER SYSTEM AT 1500 POUNDS PER SQUARE INCH ABSOLUTE.

methane-water system. Extrapolating the curve representing the L_1HL_2 equilibrium for the propylene-water system, shows that it should exist at approximately 36°F at 1500 lb/in.^{2}abs. Thus, above 36°F and below 54.7°F, the constant temperature sections will be similar to Figure 25 (b). Below 36°F the $H(L_2)L_1$ equilibrium no longer exists (Figure 25 (c)) and at approximately 31°F ice will form (Figure 25 (d)).

VI. DISCUSSION

(1) Validity of Experimental Data

Pressures were determined with an accuracy of ±0.5 lb/in.^{2} with the 1500 pound gauge and of ±5 lb/in.^{2} with the 5000 pound gauge. It is thought that the temperatures were determined with an accuracy of ±0.1°F. The hydrate equilibrium temperatures are thought to be at least within ±0.5°F of the actual equilibrium temperatures.

It is believed that the use of chromatography provided an accurate method of analysis and that vapor compositions were determined with an uncertainty of not more than 0.5%.

(2) Ethylene-Water System

Experimental data for the ethylene-water system show that the pressure-temperature gradient, of the curve representing the vapor, water-rich liquid and hydrate equilibrium in this system, becomes much greater at approximately 700 lb/in.^{2}abs. and 62.9°F. This phenomena occurs quite close to the vapor-liquid critical for pure ethylene, which exists at 748 lb/in.^{2}abs. and 49.4°F. Thus, in this region, it is possible for a phase, which was initially a gas at lower temperatures, to be compressed to such a high density that the type of behavior associated with a liquid can be expected. In a system such as the ethane-water system, where the VL_1H equilibrium exists below the vapor-liquid critical temperature, a hydrocarbon-

rich liquid phase terminates the VL_1H equilibrium and an L_1L_2H equilibrium is formed. The effect of pressure on the hydrate formation temperature for this equilibrium is much smaller than for the HL_1V equilibrium and consequently the curve representing the new equilibrium rises very quickly. Thus, a likely explanation, for the increase in slope, of the curve representing the HL_1V equilibrium in the ethylene-water system, is that the ethylene-rich phase assumes properties close to those of ethane liquid and the effect of pressure on the HL_1V equilibrium is consequently similar to the effect on the HL_1L_2 equilibrium in the ethane-water system.

Villard studied this system up to 867 lb/in.^{2}abs. and noted that the HL_1V equilibrium curve became steeper in this region. After extrapolating his data, he reported a critical decomposition temperature of 65.8°F, above which he felt hydrate would not form irrespective of the pressure of the system. An experimental investigation of the ethylene-water system up to 2000 lb/in.^{2}abs. has shown that Villard's postulate is wrong and that the slope of the equilibrium curve begins to decrease at approximately 1100 lb/in.^{2}abs. and that hydrate will form at 68.5°F at 2000 lb/in.^{2}abs.

(3) Ternary Systems

The conditions of temperature and pressure, at which hydrates will just begin to form in methane-propylene and methane-ethylene mixtures, have been defined up to 2000 lb/in.^{2}abs.

In the methane-ethylene-water system, a region exists above 700 lb/in.^{2}abs. and 62.9°F where the addition of methane to ethylene unexpectantly lowers the equilibrium pressure for hydrate formation.

A quadruple locus is present in the methane-propylene-water system. The pressure and temperature at which this four-phase equilibrium terminates depends upon the composition of the system. It terminates when the conditions of temperature and pressure are such that the vapor phase and the hydrocarbon-rich liquid phase become one homogeneous phase.

It is interesting to note that the conditions of temperature and pressure, above which hydrates will not form in either the methane-ethylene-water system or the methane-propylene-water system, are represented by practically the same curve.

(4) Solid-Vapor Equilibrium Ratios

Application of the solid-vapor equilibrium ratios to predicting hydrate forming conditions for a gas containing 64.8 mole percent CH_4, 31.8 mole percent C_2H_4 and 3.5 mole percent propylene, showed that the calculated equilibrium pressures deviated as much as 28 percent from the actual values. This indicates that the equilibrium ratios can not be used with any great dependability.

The calculated equilibrium pressures are very sensitive to the propylene concentration. In fact, the experimental hydrate forming conditions for the above mentioned mixture are essentially the same as for a methane-ethylene mixture containing 31.7 percent ethylene.

In a discussion, published with the paper (1) in which Katz presents the solid-vapor equilibrium ratios for paraffin hydrocarbons, Hammerschmidt gives experimental data for a rich gas containing approximately 40 percent methane, 18 percent ethane and 30 percent propane, plus small amounts of other hydrocarbon gases. Using the equilibrium ratios published by Katz, he also calculated the hydrate forming conditions for this gas and found that the calculated equilibrium pressures were as much as 32 percent in error. He suggested that the equilibrium ratios be used with caution for rich gases. This discrepancy between predicted and experimental values could indicate that some error does exist in the values given for the equilibrium ratios for methane or perhaps it means that the solid phase does not behave ideally.

The calculated equilibrium ratios are probably adequate for calculating hydrate forming conditions for gases rich in methane and containing only small amounts (less than 5 percent) of each of propylene and ethylene. This assumption is based on the fact that the equilibrium ratios developed by Katz work fairly well for natural gas mixtures which are very rich in methane and generally contain less than 5 percent of either ethane or propane.

For mixtures of methane, ethylene and propylene, containing greater than approximately 20 percent propylene, hydrate equilibrium points will probably fall along a four-phase equilibrium line, which can probably be approximated by the four-phase locus for the propylene-methane-water system.

VII. FUTURE WORK

Future work might include the following:

(i) A study of the systems investigated in this work at pressures greater than 2000 lb/in.^{2}abs.

(ii) Determination of the compositions of some hydrates. The composition of the hydrocarbon portion of hydrates formed in the methane-ethylene-water and methane-propylene-water systems would be useful for checking the equilibrium ratios for methane.

(iii) Determination of hydrate forming conditions for more mixtures containing ethylene and propylene. This data would be useful to further check the validity of the equilibrium ratios determined in this work.

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APPENDIX

TABLE IV

EXPERIMENTAL PRESSURE-TEMPERATURE DATA FOR METHANE-WATER

Pressure lb/in.^{2}abs.	Temperature °F	Phases
991	48.5	$H - L_1 - V$
881	46.6	
731	43.3	
708	42.6	
616	40.3	
507	36.9	
462	35.3	
412	33.0	
362	29.4	H - I - V
342	26.4	

TABLE V

EXPERIMENTAL PRESSURE-TEMPERATURE DATA FOR ETHYLENE-WATER H-L_1-V EQUILIBRIUM

Pressure lb/in.^{2}abs.	Temperature °F	Pressure lb/in.^{2}abs.	Temperature °F
1963	68.3	867	64.0
1811	67.4	809	63.7
1677	67.5	772	63.6
1474	66.4	759	63.6
1452	66.2	690	62.9
1277	65.7	656	62.3
1244	65.4	641	62.0
1090	64.8	525	59.5
1019	64.6	411	56.1
1004	64.3	306	52.1
937	64.6	201	46.1
906	64.5	143	40.7
875	64.0	96	34.7

TABLE VI

EXPERIMENTAL PRESSURE-TEMPERATURE DATA FOR PROPYLENE-WATER V-L_1-L_2 EQUILIBRIUM

Pressure lb/in.^{2}abs.	Temperature °F
160	74.1
111	48.7
104	43.7
94	37.7
91.6	36.3
85.1	31.3

TABLE VII

EXPERIMENTAL DATA FOR THREE-PHASE EQUILIBRIA, H-L_1-V, IN THE CH_4-C_2H_4-H_2O SYSTEM

Temperature °F	Pressure lb/in.^{2}abs.	Mole % C_2H_4 in Vapor (Dry Basis)	Mole % CH_4 in Vapor (Dry Basis)
56.8	1487	2.8	97.2
49.1	879	2.8	97.2
35.0	388	2.9	97.1
59.8	1485	7.6	92.4
52.7	911	7.7	92.3
35.6	334	7.7	92.3
62.8	1474	17.4	82.6
58.0	1035	17.2	82.8
50.3	590	17.2	82.8
38.7	289	17.2	82.8
66.7	1484	33.7	66.3
55.8	624	33.7	66.3
67.7	1467	45.3	54.7
63.2	944	45.0	55.0
56.0	555	44.8	55.2
38.2	183	44.9	55.1
71.3	1939	66.3	33.7
68.5	1300	65.8	34.2
64.0	803	65.8	34.2
51.6	320	65.7	34.3
69.7	1951	90.3	9.7
66.8	1101	90.0	10.0
63.7	732	89.9	10.1
53.2	320	89.8	10.2
69.3	1959	96.6	3.4
65.4	988	96.7	3.3

TABLE VIII

FOUR PHASE EQUILIBRIUM DATA FOR METHANE-PROPYLENE-WATER SYSTEM

Temperature °F	Pressure lb/in.^{2}abs.	Mole % C_3H_6 in Vapor (Dry Basis)	Mole % CH_4 in Vapor (Dry Basis)
69.3	1370	34.8	65.2
69.1	1302	31.5	68.5
68.1	1186	27.7	72.3
67.9	1181		
67.0	1182		
67.6	1100	25.7	74.3
66.4	995		
66.3	944	27.4	72.6
65.6	984		
64.8	865		
61.8	670		
60.5	605	29.4	70.6
59.2	544		
58.2	525		
55.0	398	39.0	61.0
55.0	385		
53.9	361		
52.1	309		
47.7	222	54.5	45.5
46.3	210		
41.0	143	71.0	29.0
40.9	144		

TABLE IX

EXPERIMENTAL DATA FOR THREE-PHASE EQUILIBRIA, H-L_1-V, IN THE CH_4-C_3H_6-H_2O SYSTEM

Temperature °F	Pressure lb/in.^{2}abs.	Mole % C_3H_6 in Vapor (Dry Basis)	Mole % CH_4 in Vapor (Dry Basis)
60.3	1938	0.5	99.5
54.8	977	1.4	98.6
47.4	602	1.4	98.6
34.8	257	1.5	98.5
65.3	1961	2.9	97.1
59	1100	3.4	96.6
57.1	943	2.8	97.2
48.2	496	3.2	96.8
41.3	310	3.2	96.8
35.3	205	3.3	96.7
70.2	1951	8.5	91.5
69.7	1946	8.0	92.0
67.4	1471	8.9	91.1
64.3	1090	9.0	91.0
61.6	790	9.7	90.3
54.1	474	10.3	89.7
42.1	209	10.3	89.7
34.5	127	11.3	88.7
71.3	1983	13.9	86.1
71.1	1943	12.0	88.0
68.6	1311	13.6	86.4
61	686	14.8	85.2
52.9	391	14.8	85.2
72	1991	17.9	82.1
42.4	169	23.9	76.1
73	2051	36.2	63.8
70.3	1522	34.8	65.2
71.7	1886	47.0	53.0

TABLE X

CALCULATED SOLID-VAPOR EQUILIBRIUM RATIOS FOR ETHYLENE

Pressure lb/in.^{2}abs.	Temperature °F	$y_{C_2H_4}$	y_{CH_4}	K_{CH_4}	$K_{C_2H_4}$
100	32.0	0.612	0.388	3.00	0.703
	33.0	0.660	0.340	3.04	0.743
	35.0	0.900	0.100	3.10	0.932
	35.7	1.000	-	-	1.000
150	32.0	0.324	0.676	2.43	0.448
	35.0	0.450	0.55	2.52	0.576
	40.0	0.670	0.33	2.75	0.762
	41.9	1.000	-	-	1.000
200	32.0	0.177	0.823	1.92	0.310
	35.0	0.258	0.742	2.06	0.403
	40.0	0.450	0.550	2.26	0.595
	43.1	0.600	0.400	2.37	0.722
	45.0	0.720	0.280	2.42	0.814
	46.0	0.900	0.100	2.45	0.939
	46.1	1.000	-	-	1.000
300	32.0	0.050	0.950	1.31	0.182
	35.0	0.097	0.903	1.50	0.244
	40.0	0.191	0.809	1.74	0.357
	45.0	0.377	0.623	1.90	0.561
	50.0	0.620	0.380	2.03	0.763
	51.9	0.900	0.100	2.08	0.946
	52.0	1.000	-	-	1.000
400	35.0	0.024	0.976	1.14	0.167
	40.0	0.092	0.908	1.37	0.273
	45.0	0.206	0.794	1.59	0.412
	50.0	0.390	0.610	1.73	0.603
	55.0	0.700	0.300	1.82	0.839
	55.9	1.000	-	-	1.000
500	40.0	0.035	0.965	1.16	0.208
	45.0	0.118	0.882	1.36	0.336
	50.0	0.251	0.749	1.50	0.502
	55.0	0.482	0.518	1.61	0.712
	58.3	0.750	0.250	1.66	0.883
	58.8	0.950	0.050	1.67	0.979
	58.9	1.000	-	-	1.000

TABLE X (continued ..)

Pressure lb/in.^{2}abs.	Temperature ^{o}F	$y_{C_2H_4}$	y_{CH_4}	K_{CH_4}	$K_{C_2H_4}$
600	45.0	0.063	0.937	1.21	0.279
	50.0	0.168	0.832	1.36	0.433
	55.0	0.330	0.670	1.47	0.607
	60.0	0.650	0.350	1.53	0.843
	61.1	1.000	-	-	1.000
800	50.0	0.070	0.930	1.15	0.366
	55.0	0.181	0.819	1.26	0.517
	60.0	0.390	0.610	1.33	0.720
	63.0	0.590	0.410	1.37	0.842
	63.9	1.000	-	-	1.000
1000	50.0	0.017	0.983	1.02	0.472
	55.0	0.099	0.901	1.13	0.491
	60.0	0.250	0.750	1.22	0.648
	63.0	0.400	0.600	1.26	0.763
	65.0	0.540	0.460	1.28	0.844
	66.0	0.650	0.350	1.28	0.895
	65.0	0.988	0.012	1.28	0.997
	64.6	1.000	-	-	1.000
1200	55	0.049	0.951	1.06	0.476
	60	0.162	0.838	1.14	0.613
	63	0.280	0.720	1.18	0.718
	65	0.392	0.608	1.20	0.795
	67	0.570	0.430	1.22	0.880
	67	0.930	0.070	1.22	0.987
	65.2	1.000	-	-	1.000
1500	57	0.030	0.970	1.015	0.682
	60	0.082	0.918	1.030	0.752
	63	0.170	0.830	1.050	0.809
	65	0.256	0.744	1.060	0.859
	67	0.375	0.625	1.07	0.903
	68	0.480	0.520	1.07	0.933
	70	0.700	0.300	1.08	0.969
	68	0.965	0.035	1.07	0.998
	66.5	1.000	-	-	1.000

TABLE X (continued ..)

Pressure lb/in.^{2}abs.	Temperature °F	$y_{C_2H_4}$	y_{CH_4}	K_{CH_4}	$K_{C_2H_4}$
2000	63	0.066	0.934	1.005	0.777
	65	0.120	0.880	1.030	0.822
	67	0.194	0.806	1.040	0.862
	68	0.278	0.722	1.045	0.902
	70	0.490	0.510	1.050	0.972
	70	0.860	0.140	1.050	0.992
	68.2	1.000	-	-	1.000
3000	67	0.035	0.965	1.015	0.720
	68	0.076	0.924	1.020	0.808
	70	0.228	0.772	1.025	0.923
	72.2	0.658	0.342	1.030	0.986

TABLE XI

CALCULATED SOLID-VAPOR EQUILIBRIUM RATIOS FOR PROPYLENE

Pressure lb/in.^{2}abs.	Temperature °F	$y_{C_3H_6}$	y_{CH_4}	K_{CH_4}	$K_{C_3H_6}$
100	32.0	0.119	0.881	3.00	0.169
	35.0	0.200	0.800	3.11	0.269
	36.1	0.500	0.500	3.13	0.595
	36.1	0.900	0.100	3.13	0.930
150	32.0	0.041	0.959	2.43	0.0678
	35.0	0.075	0.925	2.52	0.118
	40.0	0.164	0.836	2.75	0.236
	42.0	0.450	0.550	2.70	0.566
200	32.0	0.018	0.982	1.92	0.0369
	35.0	0.034	0.966	2.06	0.0638
	40.0	0.083	0.917	2.26	0.140
	45.0	0.270	0.730	2.42	0.390
	45.7	0.580	0.420	2.44	0.700
300	35.0	0.008	0.992	1.50	0.0236
	40.0	0.028	0.972	1.74	0.0635
	45.0	0.068	0.932	1.90	0.134
	50.0	0.200	0.800	2.03	0.330
	51.3	0.460	0.540	2.06	0.623
400	40.0	0.009	0.991	1.37	0.0325
	45.0	0.030	0.970	1.59	0.077
	50.0	0.078	0.922	1.73	0.167
	55.0	0.387	0.613	1.82	0.583
500	45.0	0.015	0.985	1.36	0.0543
	50.0	0.043	0.957	1.50	0.119
	55.0	0.105	0.895	1.61	0.236
	58.0	0.337	0.663	1.66	0.561
600	45.0	0.007	0.993	1.21	0.0391
	50.0	0.026	0.974	1.36	0.0915
	55.0	0.062	0.938	1.47	0.171
	60.0	0.200	0.800	1.53	0.418
	60.3	0.300	0.700	1.53	0.553
800	55	0.030	0.970	1.26	0.134
	60.0	0.082	0.918	1.33	0.266
	63.8	0.264	0.736	1.37	0.570

TABLE XI (continued ..)

Pressure lb/in.^{2}abs.	Temperature °F	$y_{C_3H_6}$	y_{CH_4}	K_{CH_4}	$K_{C_3H_6}$
1000	55.0	0.014	0.986	1.13	0.110
	60.0	0.050	0.950	1.22	0.225
	65.0	0.128	0.872	1.28	0.402
	66.7	0.253	0.747	1.29	0.602
1200	55.0	0.005	0.995	1.06	0.0807
	60.0	0.030	0.970	1.14	0.200
	65.0	0.083	0.917	1.20	0.352
	68.3	0.250	0.750	1.23	0.641
1500	60.0	0.014	0.986	1.03	0.325
	65.0	0.053	0.947	1.065	0.477
	69.0	0.120	0.880	1.07	0.674
	70.0	0.177	0.823	1.07	0.766
2000	62.5	0.010	0.990	1.02	0.345
	65.0	0.023	0.977	1.025	0.426
	69.0	0.062	0.938	1.045	0.601
	70.0	0.080	0.920	1.05	0.646
	71.8	0.150	0.850	1.05	0.785
3000	67.4	0.010	0.990	1.015	0.417
	69.0	0.018	0.982	1.020	0.473
	70.0	0.028	0.972	1.025	0.549

TABLE XII

COMPARISON OF CALCULATED WITH EXPERIMENTAL CONDITIONS FOR HYDRATE FORMATION

Gas Composition: 64.8 mole % CH_4
31.7 mole % C_2H_4
3.5 mole % C_3H_6

Temperature °F	Hydrate Formation Pressure lb/in.^{2}abs.		Percent Deviation
	Calculated	Experimental	
66.9	1398	1941	28.0
65.1	1178	1533	23.1
61.0	790	1044	24.3
60.9	-	1031	-
58.6	654	831	21.3
48.9	341	430	20.7

Sample Calculations

(1) Calculation of Equilibrium Ratios

System: Methane-Ethylene-Water

Equilibrium Pressure: 500 lb/in.^{2}abs.

Equilibrium Temperature: 50°F

Vapor Phase Composition: $y_{CH_4} = 0.749$

$y_{C_2H_6} = 0.251$

K_{VS} for CH_4 at 500 lb/in.^{2}abs. and 50°F (Figure 8) = 1.50

At the equilibrium point $\Sigma \frac{y}{K} = 1$

Therefore
$$\frac{y_{C_2H_6}}{K_{C_2H_6}} = 1 - \frac{y_{CH_4}}{K_{CH_4}}$$

$$\frac{0.251}{K_{C_2H_6}} = 1 - \frac{0.749}{1.50}$$

$$= 0.501$$

$$K_{C_2H_6} = \frac{0.251}{0.501}$$

$$= 0.502$$

The solid-vapor equilibrium ratio for ethylene is 0.502 at 500 lb/in.^{2}abs. and 50°F.

(2) Prediction of Conditions for Hydrate Formation

Component	Mole Fraction in the Gas (y)	K for the Component at 58.6°F and 600 psia	y/K or x
CH_4	0.648	1.52	0.427
C_2H_4	0.317	0.775	0.409
C_3H_6	0.035	0.305	0.115
	1.000		0.951

The assumed pressure of 600 lb/in.^{2}abs. is low therefore try 700 lb/in.^{2}abs.

CH_4	0.648	1.41	0.459
C_2H_4	0.317	0.720	0.441
C_3H_6	0.035	0.248	0.141
	1.000		1.041

700 lb/in.^{2}abs. is too high since $\sum \frac{y}{K}$ is greater than unity.

Interpolation between this and the previous result gives a value of 654 lb/in.^{2}abs.

The experimental equilibrium pressure at 58.6°F was 831 lb/in.^{2}abs.

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